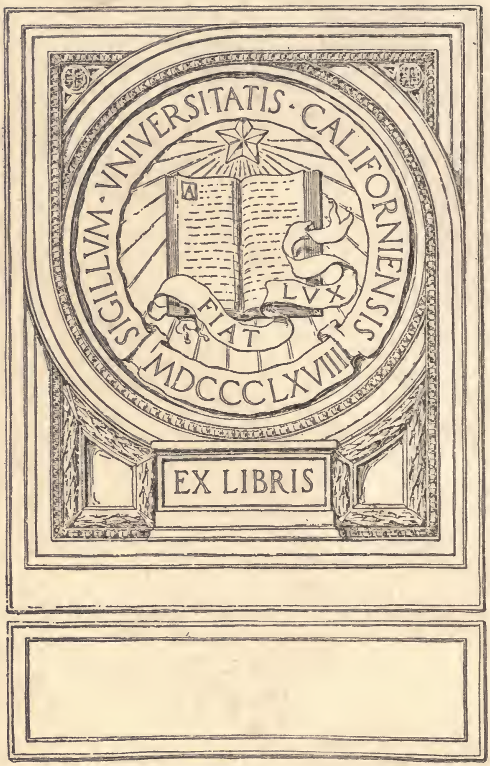

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PROBLEMS IN PHYSICAL CHEMISTRY

PROBLEMS IN PHYSICAL CHEMISTRY

WITH PRACTICAL APPLICATIONS

BY

EDMUND B. R. PRIDEAUX, M.A., D.Sc.

ASSISTANT LECTURER IN EDUCATION, UNIVERSITY OF LIVERPOOL
FORMERLY LECTURER IN CHEMISTRY, HERIOT-WATT COLLEGE, EDINBURGH

UNIV. OF
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PREFACE

Some twenty-five years ago there appeared certain excellent books dealing with "Chemical Arithmetic." They served, and doubtless still serve, a very useful purpose in familiarising students of chemistry with the fundamental laws of their science, and in teaching them how to think in a quantitative and accurate manner. The great advances made by physical chemistry during the last quarter of a century have, however, created a new chemical arithmetic. Probably every teacher of physical chemistry has felt the need of a suitable book on this subject. I suggested, therefore, to Dr. Prideaux a year or two ago that he might undertake to fill this gap in our scientific literature.

In order to gain some practical experience of the needs and capacities of students in this respect, he conducted a very successful "problem class" in connection with my lectures to senior students at Liverpool University. The fruits of this experience and knowledge are contained in the present volume, which ranges practically over the whole field of physical chemistry. Dr. Prideaux has carried out this work in an admirable manner, so that his book may be warmly recommended to all chemists, physicists and engineers who desire to obtain a grasp of the fundamental quantitative principles of modern chemical science.

F. G. DONNAN.

Muspratt Laboratory of Physical
and Electro-Chemistry.
March, 1912.

AUTHOR'S PREFACE

The aim of the present work is to provide a series of arithmetical examples which shall illustrate the more important developments of Physical Chemistry. The concepts and approximation methods which have introduced some degree of order into the phenomena grouped under this head will, it is hoped, gain in definition and practical utility if they are used as required for the solution of numerical problems.

A previous knowledge of the fundamental chemical laws, as well as the meaning of elementary physical magnitudes and operations, has been assumed throughout.

The physical problems which have been included are such as possess a particular importance for the physico-chemical investigator and technical chemist. For the sake of convenience, the problems have been arranged in sections, each preceded by a brief introduction. The introductions are necessarily short, and include only such summarised information as is necessary for an intelligent working of the problems. The information conveyed being, from the nature of the case, not always sufficient for a complete solution, supplementary hints or specimen problems have been added where required.

Subject to these limitations the whole work has been made, as far as possible, progressive in character, sufficient knowledge for the solution of each problem being contained in the preceding sections. The aim being to illustrate and assist in further reading, rather than to supply examination puzzles, the choice of problems has been restricted to such as can be solved by the aid of general principles and elementary mathematics. A multiplication of details has been avoided, except in some cases where the simple laws which it is desired to emphasise are immediately applicable to some practical problem.

A few mathematical formulæ frequently employed and tables of logarithms have been added in order to make the work as self-contained as possible.

Since a complete abstract of the researches and theory upon which the problems are founded is out of the question, numerous references to the original papers have been included in the text. The principle of priority has been largely used as a guide in the selection of researches, especially in cases where the earlier researches, though not, perhaps, as full and accurate as the later, yet possess an equal educational value.

The following books have been found particularly useful in dealing with the whole or separate departments of the subject:—

Handbuch der Anorganische Chemie (Abegg).

Theoretische Chemie (Nernst).

Lectures in Theoretical and Physical Chemistry (Van't Hoff, transl. Lehfeldt).

Studies in Chemical Dynamics (Van't Hoff, Cohen, transl. Ewan).

Thermodynamics of Technical Gas Reactions (Haber, transl. Lamb).

Die Chemische Affinität und Ihre Messung (Sackur).

Lehrbuch der Allgemeine Chemie (Ostwald).

Thermodynamics and Chemistry (Nernst).

Theory of the Lead Accumulator (Dolezalek, transl. von Ende).

Metallurgical Calculations (Richards).

Heat Energy and Fuels (v. Juptner).

Physical Chemistry (Lehfeldt).

Text-books of Physical Chemistry (Ramsay's Series).

Leitvermögen der Elektrolyte (Kohlrausch).
Experimentelle Unter suchungen von Gasen (Travers).
Physical Chemistry (Ewell).
Physiko-Chemische Messungen (Ostwald-Luther).

I wish to place on record my indebtedness to Professor Donnan for his ever ready advice and criticism, and his kind interest throughout the preparation of this work.

I should also like to take this opportunity of thanking the students of Liverpool University, who by attending a problem class, have supplied an additional incentive to convert the somewhat prolix results of research into a form suitable for teaching.

E. B. R. PRIDEAUX.

March, 1912.

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PROBLEMS IN PHYSICAL CHEMISTRY

Mathematical Methods and Formulæ for Reference.

Calculations.

The following numerical calculations can be made, in most cases, with the aid of the included table of four figure logarithms. There are many examples for the solution of which a slide rule is sufficiently accurate, while, in a few instances, the use of six or seven figure logarithms is desirable.

The methods of shortened multiplication and division, which are described in most text-books of practical physical chemistry or modern arithmetic may be used, if desired. Each calculation should be carried out up to and including the first uncertain figure, but no further.

A simplification may be effected whenever the second term in the expression $1 \pm h$ is so small that its second power may be neglected, in comparison with the first term (within the limits of the accuracy aimed at).

Powers, products, or quotients of this expression may be approximately obtained by including only the first and second terms of the expansion

$$(1 \pm h)^n = 1 \pm nh$$

$$\sqrt{1 + h} = 1 + \frac{h}{2}$$

$$\frac{1}{1 + h} = 1 - h$$

$$\frac{(1 \pm h_1)(1 \pm h_2)}{(1 \pm h_3)(1 \pm h_4)} = 1 \pm h_1 \pm h_2 \mp h_3 \mp h_4$$

Hence, prove that:—

$$\sqrt{10\,(10+h)} = \frac{10+10+h}{2},$$

i.e., if the difference between two numbers is small compared to each of them, the geometrical mean is approximately equal to the arithmetical mean.

The theory of proportional differences is an application of Taylor's theorem.

If a number be increased by a small fraction of itself, the increase in the number is nearly proportional to the increase in the natural logarithm of the number.

$$\log_e (N+h) - \log_e N = \frac{h}{N}$$

Equations of a higher degree than the second have in all cases been avoided. The general solution of quadratic equations will be found useful

$$ax^2 + bx + c = o$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Logarithms.

If $e^x = a$

$x = log_e\, a$ the logarithm of a to the base e.

The base of the natural system of logarithms

$$e \doteq 2{\cdot}7183 = \Sigma\left(1 + \frac{1}{1 \times 2} + \frac{1}{1 \times 2 \times 3} \quad . \quad .\right)$$

$$10^x = a,\ x = \log_{10} a$$

x is now the common or decimal logarithm of a (to the base 10).

$$\log_e\ a = \log_{10} a \times \log_e 10$$

$$\log_e 10 = 2{\cdot}3026$$

In physico-chemical calculations, the function $\log_e x$ $\left(\int \frac{dx}{x}\right)$ is frequently encountered. It has been written as log x, the usual meaning of $\log_{10} x$ being retained and the multiplying factor 2·3026 being understood.

$$\begin{aligned}
\log ab &= \log a + \log b \\
\log \frac{a}{b} &= \log a - \log b \\
\log a^n &= n \log a \\
\log a^{-n} &= -\, n \log a
\end{aligned}$$

$$\begin{aligned}
\log\ \ 2 &= 0{\cdot}3010 \text{ from tables} \\
\log\ 2000 &= \log 1000 + \log 2 = 3{\cdot}3010 \\
\log 0{\cdot}002 &= \bar{3}{\cdot}3010, \text{ etc.}
\end{aligned}$$

$$\begin{aligned}
\text{anti-log } 0{\cdot}2940 &= 1{\cdot}968 \\
\text{,,} \quad \text{,,} \quad 3{\cdot}2940 &= 1968, \text{ etc.}
\end{aligned}$$

Differentials.

The variables are denoted by x, y, z; numerical indices (which may be negative or fractional) by n, numerical coefficients and other constants by K.

$$\frac{dx^n}{dx} = nx^{n-1} \quad . \quad . \quad . \quad . \quad . \ (1)$$

$$\frac{dK}{dx} = 0, \ \frac{dx}{dx} = 1$$

$$\frac{d\,(K + x)}{dx} = \frac{dK}{dx} + \frac{dx}{dx} = 1 \quad . \quad . \quad . \quad . \ (2)$$

$$\frac{d\,(xy)}{dz} = x\frac{dy}{dz} + y\frac{dx}{dz} \quad . \quad . \quad . \quad . \ (3)$$

$$\begin{aligned}
\frac{d\left(\dfrac{y}{x}\right)}{dz} &= \frac{d\,(yx^{-1})}{dz} = \frac{yd(x^{-1})}{dz} + \frac{x^{-1}dy}{dz} \quad \text{by (8)} \\
&= -\,\frac{ydx}{x^2dz} + \frac{1dy}{xdz} \ by\ (1) \\
&= \frac{x\dfrac{dy}{dz} - y\dfrac{dx}{dz}}{x^2} \quad . \quad . \quad . \ (4)
\end{aligned}$$

$$\frac{d(Kx)}{dx} = K \quad . \quad . \quad . \quad . \quad \text{from (3)}$$

$$\frac{d\log_e x}{dx} = \frac{1}{x}, \frac{d\log_{10}x}{dx} = \frac{0{\cdot}4343}{x}$$

$$\frac{d\log(xy)}{dz} = \frac{d\log x}{dz} + \frac{d\log y}{dz}$$

If x and y are two variables dependent upon one another (such as pressure and temperature, concentration and time), and y (the dependent variable) is known as a function $f(x)$ of x (the independent variable), then by the laws of differentiation the rate of change of y with x may be expressed as another function $f'(x)$ of x.

Thus: $$\frac{dy}{dx} = \frac{d(fx)}{dx} = f'(x) \quad . \quad . \quad . \quad (1)$$

e.g., if $y = x^2$, the rate of change of y at any given value of x is equal to $2x$. See equation (1) above. An example of the application is given by the differential heat of solution, etc., on pp. 32, 33.

Integrals.

The meaning of the process of integration is easily seen after the graphical and quantitative treatment of experimental data. The numerical value of the integral $\int ydx$ is often required; y being some known function $f(x)$ of x.

It is necessary in the first place to find another function $f'(x)$, such that—

$$d\,\frac{f'(x)}{dx} = f'(x) = y$$

It follows by the rules of integration that—

$$\int d f'(x) = f'(x) + C_i = \int f(x)\,dx = \int ydx$$

For example, let $y = x^n$ and suppose that it is required to evaluate the integral $\int ydx$ between the limits x_1 and x_2.

Then since $\frac{d}{dx}\left(\frac{1}{n+1}x^{n+1} + C_i\right) = x^n$ by equation (1) above,

$$\int y dx = \int x^n\, dx = \frac{1}{n+1}\, x^{n+1} + C_i \quad . \quad . \ (1)$$

$$\int_{x_1}^{x_2} x^n dx = \frac{1}{n+1}\,(x_2{}^{n+1} - x_1{}^{n+1})$$

Thus, if $y = x^2$

$$\int_{x_1}^{x_2} y dx = \tfrac{1}{3}\,(x^3{}_2 - x^3{}_1)$$

The following table comprises such standard integrals as are required for simple physico-chemical calculations. The integration constant is understood in all cases.

Differential Calculus.	*Integral Calculus.*
$\frac{dx_n}{dx} = nx^{n-1}$	$\int x^n\, dx = \frac{x^{n+1}}{n+1} \quad . \quad . \ (1)$
$\frac{da^x}{dx} = a^x \ \log^e\ a$	$\int a^x\, dx = \frac{a^x}{\log_e\ a} \quad . \quad . \ (2)$
$\frac{d(e^x)}{dx} = e^x$	$\int e^x\, dx = e^x \quad . \quad . \quad . \ (2)$
$\frac{d \log_a\ x}{dx} = \frac{1}{x} \log_a\ e$	$\int \frac{dx}{x} = \frac{\log_a\ x}{\log_a\ e}$ or $\log_a\ x \,.\, \log_e\ a$ or $\log_e\ x \quad . \quad . \quad . \ (3)$

Further integrals may be desired as required from these standard forms and the laws of differentiation.

Thus from (1) by the substitution of $-n$ for n :—

$$\int \frac{dx}{x^n} = \frac{1}{1-n} \cdot \frac{1}{x^{n-1}}$$

From (2) p. 3.

$$\frac{d(a-x)}{dx} = -1,\ d(a-x) = -dx$$

$$\therefore \frac{dx}{a-x} = -\frac{d(a-x)}{a-x}$$

∴ From (3) above :—

$$\int \frac{dx}{a-x} = -\log (a-x)$$

It may also be shown that :

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{a-b} \log \frac{b(a-x)}{a(b-x)}$$

The following are the principal symbols employed throughout this work.

Current usage and the conventions adopted by national and international agreement have been adopted wherever there has been unanimity. A few changes have been rendered necessary to avoid the use of the same symbol for different ideas.

The subscripts added to the main symbols are explained whenever their meaning is not obvious.

SYMBOLS.

General and Mechanical Symbols.

l	Length ; cm. = centimetres ; mm. = millimetres ; $\mu = 0{\cdot}001$ mm.
m	Mass.
w, W	Weight.
t	Time.
s	Area ; $(\text{cm.})^2$ = square centimetres.
v	Volume ; c.c. = cubic centimetres.

Physical and Chemical Symbols.

c, C	Concentration (mols. per litre).
η	Concentration (mols. per c.c.).
D, Δ	Density, in grams per c.c,
V	Volume ; dilution (litres per gram equivalent).
mol. M, m . .	The gram molecule, or molecular weight expressed in grams.

N	Number of mols.
n	Valency; coefficient of stoichiometrical equation.
t°	Temperature Centigrade.
T°	Temperature absolute.
a, b, c.	First, second, third terms of a power series.
p	Pressure (general, gas, and partial gas).
P	Total pressure of a gas mixture; osmotic pressure.
R	The gas constant.
p_c, v_c, T_c	The critical constants.
$N. T. P.$	Normal temperature and pressure (0° C. and 760 mm. of mercury).
$N.$	Normal concentration (gram equivalents per litre).
$0.1N.$, $\frac{N}{100}$, etc.	Decinormal, centinormal, etc.
$aq.$	Excess of water.
K	A constant; the equilibrium constant.
K_p, K_c	Equilibrium constant at constant pressure and constant volume.
k	Velocity constant.
$[A]$	The concentration of the molecular species A.
C_i	Integration constant; chemical constant.

Energy Symbols.

Q	Quantity of heat in general, or "reversible heat."
q	Calorimetric heat; change of intrinsic energy.
U	Internal or total energy.
A	Free energy; change of free energy.
Q_{LV}, Q_{SL} λ	Latent heats of vaporisation and fusion.

J, E	Intensity of radiation ; total radiation.
h, H	Specific and molecular heat $\left(\frac{d\,Q}{dt^{\circ}}\right)$.
h_m, H	Mean specific and molecular heats.
h_p, h	Specific heat at constant pressure and at constant volume.
$v = \frac{H_p}{H_v}$	Adiabatic constant of gas.
cal.	Gram calorie (as defined p. 10).
Kal.	Kilogram calorie.
j, Kj	Joule ; kilojoule.

Electrochemical Symbols.

I	Current.
R, r	Resistance.
κ	Conductivity.
Λ	Equivalent conductivity.
Λ_0	Equivalent conductivity at infinite dilution.
a	Degree of dissociation.
ν_A, ν_K	Transport number of anion and kation.
U_A, U_K	Absolute ionic velocities in cm. per second under a potential gradient of 1 volt per cm.
$\left.\begin{matrix} L_A, L_K \\ l_A, l_K \end{matrix}\right\}$	Ionic conductivities (see p. 179).
u_A, u_K	Apparent ionic velocity at incomplete dissociation.
$[H^{\cdot}], [Cl']$	Concentration of hydrogen ion and of chlorine ion.
$+ \quad -$	Charge on a gram kation and a gram anion.
E. or *E.M.F.*	Electromotive force of a cell.
e	Single potential at an electrode.
e_0	Normal potential as defined p. 236.

For further definitions, and the relations of these units to one another, see p. 173.

UNITS AND STANDARDS.

Dimensions of Units.

l (length) m (mass) t (time) w (weight)

Velocity $= l\, t^{-1}$

Acceleration $= l\, t^{-2}$

Force $= m\, l\, t^{-2}$

Work $= m\, l^2\, t^{-2}$

Power $= m\, l^2\, t^{-3}$

Heat = work (× constant); see p. 11.

Volume, v $= l^3$. Area, $S = l^2$

Density $= w\, v^{-1}$; w = weight (see below).

Specific volume $= w^{-1}\, v$

Pressure $= w\, l^{-1}\, t^{-2}$

If the units of length, mass and time chosen are the centimetre, gram (as defined below), and the second, then the above derived units are expressed as "absolute" or C.G.S. units.

Metric System.

Sub-divisions of the units are distinguished by the prefixes deci-, centi-, milli-, meaning $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$.

Multiples of the units are distinguished by the prefixes deca-, hecto-, kilo, meaning 10, 100, and 1,000 times.

Length. The centimetre is $\frac{1}{100}$ of the distance (metre) between two marks on a standard bar of platinum, as measured under certain specified conditions.

Mass, defined by means of the weight in a given locality. The metric unit is $\frac{1}{1000}$ part of a standard mass of platinum (the kilogram).

Weight. The weight of a given mass is the force with which it is attracted by the earth. This force exerted on a mass of 1 gram at sea-level, and latitude 45°, is 980·6 dynes (see below). A volume of 1 decimetre cube of pure water at the temperature of its maximum density weighs 0·999,955 ± 0·00002 kilograms.

Volume.

The litre is the volume occupied by the mass of 1 kilogram of pure water at a pressure of 1 atmosphere as defined below, and the temperature of maximum density = 4° C.

The cubic centimetre is $\frac{1}{1000}$ part of the litre.

By definition, therefore, the density of water in grams per cubic centimetre = 1 at 4° C.

Litre (Mohr's) is the volume of 1 kilogram of distilled water, weighed with brass weights in air, at 15° C., and under a pressure of 1 atmosphere.

Force and Work.

The dyne is the force which in 1 second imparts to a mass of 1 gram a velocity of 1 centimetre per second.

Erg. The work done by a force of 1 dyne acting through a length of 1 centimetre, in the direction of the force.

Practical Units.

Gravity constant (acceleration)—

$$g = g_{45} (1 - 0{\cdot}002644 \cos \phi + 0{\cdot}0_5 7 \cos^2 2 \phi - 0{\cdot}0_3 3086 H$$

$$g_{45} = 980{\cdot}617 \text{ at sea-level, at } 45^\circ \text{ N. latitude.}$$

ϕ = the latitude in degrees. H = height above sea-level (in metres).

Therefore 1 gram weight under the above conditions = 980·617 dynes.

Standard Atmosphere. The pressure due to a column of mercury 760 millimetres high, at 0° C., at sea-level and latitude 45°.

The standard atmosphere is equal to $1{\cdot}0133 \times 10^6$ dynes per $(\text{cm.})^2$ (see Problem 6, p. 16).

Gram Calorie. The amount of heat required to raise 1 gram of water from 14°·5 to 15°·5.

Kilogram Calorie. The amount of heat required to raise 1 kilogram of water from 14°·5 to 15°·5.

British Thermal Unit. The amount of heat required to raise 1 lb. of water 1° F. at 60° F.

Pound Calorie, defined as the gram calorie, the weight of water being 1 lb.

The following units of work and energy are derived from the gravity constant given above.

Gram Centimetre. The work done when 1 gram is brought through a distance of 1 centimetre against the gravitational force.

Kilogram Metre is defined similarly. The weight is 1 kilogram, the distance through which it is moved is 1 metre. Therefore 1 kilogram metre = 1×10^5 gram centimetre.

Joule = volt × coulomb (see p. 12).
= $10^8 \times 10^{-1}$ C.G.S. units.

Kilojoule = 1,000 joules.

Watt = 1 joule per second.

Board of Trade Unit
Kilowatt hour . } = 1,000 × 3,600 watts.

Foot-lb. second = 453·6 × 981 × 30·49.
= 1·357 watts.

Horse-power = 550 foot-lb. seconds.
= 550 × 1·357 = 746 watts.
= 0·746 kilowatts.

Conversion Table.

	Erg.	Joule Watt-Sec.	15° Cal.	Litre Atmospheres.	Kilogram-metre.
1 Erg.	—	10^{-7}	$2{\cdot}389 \times 10^{-8}$	$9{\cdot}869 \times 10^{-10}$	$1{\cdot}019 \times 10^{-8}$
Joule	10^7	—	$2{\cdot}389 \times 10^{-1}$	$9{\cdot}869 \times 10^{-3}$	$1{\cdot}019 \times 10^{-1}$
Calorie	$4{\cdot}185 \times 10^7$	4·185	—	$4{\cdot}131 \times 10^{-2}$	$4{\cdot}268 \times 10^{-1}$
Litre Atm.	$1{\cdot}0133 \times 10^9$	$1{\cdot}0133 \times 10^2$	$2{\cdot}420 \times 10$	—	$1{\cdot}033 \times 10$
Kg. metre	$9{\cdot}806 \times 10^7$	9·806	2·343	$9{\cdot}678 \times 10^{-2}$	—
R (Universal gas constant)	$8{\cdot}317 \times 10^7$	8·317	1·987	$8{\cdot}209 \times 10^{-2}$	$8{\cdot}482 \times 10^{-1}$

Electrical Units.

Quantity.

Coulomb (see Ampere) = 1×10^{-1} absolute (C.G.S.) electro-magnetic units.

Faraday = 96,540 coulombs.

The amount of electricity required to set free 1 gram equivalent at each electrode when a current is passed through an electrolytically conducting material.

One coulomb deposits 0·00118 gram of silver in a silver voltameter.

Current.

A conductor through which electricity passes at the rate of 1 coulomb per second is said to carry a current of 1 ampere.

Ampere = 1 coulomb per second.

Resistance.

The **ohm** is the resistance at 0° of a column of mercury, having a length of 106·3 centimetres at 0°, and a uniform cross-section of 1 square millimetre.

The weight of the mercury is 14·4521 grams. One ohm = 1×10^9 absolute units.

Siemens' mercury unit, used in some earlier accounts of physico-chemical investigations, is the resistance at 0° of a column of mercury, having a length of 100 centimetres, and a uniform cross-section of 1 square millimetre.

Conductivity (reciprocal ohms) is the reciprocal of resistance (ohms).

Volt. When a homogeneous conductor having a resistance of 1 ohm carries a current of 1 ampere, the difference of potential between the ends of the conductor is 1 volt.

One volt = 10^8 C.G.S. units.

Ohm's Law. By the above definitions, it follows that if I is the current in amperes, E the electromotive force in volts, and R the resistance in ohms: $I = \frac{E}{R}$.

Electromotive Force is expressed in volts. The practical standard of electromotive force is a cell composed of standard materials. The cell adopted as the international standard is the Weston normal element.

The electrodes are cadmium amalgam and mercury. The solution is saturated with respect to $Cd\ SO_4 + \frac{8}{3} H_2O$ and $Hg_2\ SO_4$.

The electromotive force E_t of this element at any temperature $t°$ is obtained from that at 20°, by the following formula:

$$E = 1{\cdot}0183 \pm 0{\cdot}0001 \text{ at } 20°.$$

For the usual laboratory temperature the Jaeger and Wachsmuth temperature coefficient gives correct results.

$$E_t = E - 0{\cdot}0_438\,(t - 20) - 0{\cdot}0_665\,(t - 20)^2.$$

For higher temperatures the formula recommended by the Bureau of Standards is more exact.

$$E_t = E - 0{\cdot}0_4406\,(t - 20) - 0{\cdot}0_695\,(t - 20)^2 + 0{\cdot}0_71\,(t - 20)^3.$$

INTERNATIONAL ATOMIC WEIGHTS, 1911.

Symbol.	Element.	Atomic Weight.	Symbol.	Element.	Atomic Weight.
Ag	Silver	107·88	Co	Cobalt	58·97
Al	Aluminium	27·1	Cr	Chromium	52·0
Ar	Argon	39·88	Cs	Caesium	132·81
As	Arsenic	74·96	Cu	Copper	63·57
Au	Gold	197·2	Dy	Dysprosium	162·5
B	Boron	11·0	Er	Erbium	167·4
Ba	Barium	137·37	Eu	Europium	152·0
Be	Beryllium	9·1	F	Fluorine	19·0
Bi	Bismuth	208·0	Fe	Iron	55·85
Br	Bromine	79·92	Ga	Gallium	69·9
C	Carbon	12·00	Gd	Gadolinium	157·3
Ca	Calcium	40·09	Ge	Germanium	72·5
Cd	Cadmium	112·40	H	Hydrogen	1·008
Ce	Cerium	140·25	He	Helium	3·99
Cl	Chlorine	35·46	Hg	Mercury	200·0

INTERNATIONAL ATOMIC WEIGHTS—*continued.*

Symbol.	Element.	Atomic Weight.	Symbol.	Element.	Atomic Weight.
In	Indium	114·8	Rb	Rubidium	85·45
Ir	Iridium	193·1	Rh	Rhodium	102·9
I	Iodine	126·92	Ru	Ruthenium	101·7
K	Potassium	39·10	S	Sulphur	32·07
Kr	Krypton	82·9	Sb	Antimony	120·2
La	Lanthanum	139·0	Sc	Scandium	44·1
Li	Lithium	6·94	Se	Selenium	79·2
Lu	Lutetium	174·0	Si	Silicon	28·3
Mg	Magnesium	24·32	Sm	Samarium	150·4
Mn	Manganese	54·93	Sn	Tin	119·0
Mo	Molybdenum	96·0	Sr	Strontium	87·63
N	Nitrogen	14·01	Ta	Tantalum	181·0
Na	Sodium	23·00	Tb	Terbium	159·2
Nb	Niobium	93·5	Te	Tellurium	127·5
Nd	Neodymium	144·3	Th	Thorium	232·4
Ne	Neon	20·2	Ti	Titanium	48·1
Ni	Nickel	58·68	Tl	Thallium	204·0
O	Oxygen	16·000	Tm	Thulium	168·5
Os	Osmium	190·9	U	Uranium	238·5
P	Phosphorus	31·04	V	Vanadium	51·06
Pb	Lead	207·10	W	Tungsten	184·0
Pd	Palladium	106·7	Xe	Xenon	130·2
Pr	Praseo-		Y	Yttrium	89·0
	dymium	140·6	Yb	Ytterbium	172·0
Pt	Platinum	195·2	Zn	Zinc	65·37
Ra	Radium	226·4	Zr	Zirconium	90·6

PROBLEMS.

Units and Standards.

1. What is the relation between the centimetre cube and the cubic centimetre, as defined on p. 10.

Answer 1 cubic centimetre is equal to
1·000045 centimetre cube.

2. A flask contains 1 kilogram of water at 15° C., weighed in air, against brass weights. What is the volume of the flask in litres? D_{15} (water) $=$ 0·999126 D_{15} (air) $=$

$0{\cdot}0_2 1214$ D_{15} (brass) $= 8{\cdot}0$. If $w_0 =$ the weight of the water in a vacuum, $w =$ the weight of the water against the brass weights in air.

$$W_0 = W\left(1 + \frac{D\,(\text{air})}{D\,(\text{water})} - \frac{D\,(\text{air})}{D\,(\text{brass})}\right).$$

Answer Vol. of flask $= \dfrac{W_0}{D_{15}} =$ **1001·94** c.c..

3. A molar normal solution of KCl being defined as one containing 74·59 grams in one litre of solution at 18°; what is the percentage error committed if 74·59 grams, weighed against brass weights in air, be made up to a litre at 15° C.? (The expansion of 1 litre of such a solution may be taken over this range as 0·3 c.c. per degree and $D_{KCl} = 2{\cdot}0$).

Calculate W_0 the absolute weight at 15° of the salt as above, and find the volume assumed by the litre originally measured at 15° when it is heated to 18°.

Answer The two errors tend to neutralise one another, and the percentage error is — **0·044.**

4. How many grams of water weighed against brass weights at 15° will occupy the volume of a true litre?

By definition 1 true litre measured at 4° weighs 1,000 grams; therefore, if measured at 15°, it weighs $1000 \times D_{15}$ grams (absolute weight in a vacuum).

From this, the weight in air against brass weights can be found as in Problem 2, p. 14.

Answer **998·063** grams.

Show that this result can at once be obtained from Problem 2.

5. In one of Joule's original experiments the heat capacity of the calorimeter was 6,316 calories per degree.

Two weights, each falling 20 times through a distance of 160·5 centimetres were used to stir the water of the calorimeter, the energy of falling being thereby converted into heat. The combined mass of the weights was 26,320 grams, and the rise of temperature of the calorimeter was 0°·313. Find the value of the calorie in ergs ($g = 981$).

Answer 1 calorie = **41·9** × **10**^{6} ergs.

The result is obviously obtained by calculating the ratio of the work done by gravity (in ergs) to the heat evolved (in calories). Edser ("Heat," p. 277).

6. If the density of mercury is 13·596 at 0°, what is the force of normal atmospheric pressure (760 mm. of mercury) in dynes per (cm.)^2, and in grams per (cm.)^2?

Answer **1·0133** × **10**^{6} dynes per (cm.)^2.
10,333 grams per (cm.)^2.

7. A litre atmosphere is the work done by a gas when it expands by 1 litre against a pressure of 1 atmosphere per (cm.)^2. What is the value of a litre atmosphere in ergs and in gram centimetres?

Answer **1·0133** × **10**^{9} ergs.
1·0333 × **10**^{6} gram centimetres.

Work $= pv = p \times 10^3$,
p having the values found in the last problem.

8. From the preceding, and the value of the calorie in ergs (Table, p. 16) verify the relation: 1 litre atmosphere = **24·20** calories.

9. The coefficient of expansion of mercury between 0° and 100° is 0·00018, and the heat required to raise 1 gram from 0° to 100° is 3·3 calories (at a constant pressure of 1 atmosphere).

What fraction of the total energy expended in raising the temperature of 1 gram of mercury from 0° to 100° is utilised as mechanical work?

Answer $\mathbf{0{\cdot}0_797}$ of the whole energy is spent in overcoming external pressure.

The increase in the volume of 1 gram may be converted into litre atmospheres at once, then into calories by the factor on p. 11.

For the density of mercury, see Problem 6, above.

10. By means of the definitions of the erg and of the electrical units determine the value of the joule and the kilowatt in ergs and in ergs per second.

Answer 1 joule = 10^7 ergs.
1 kilowatt = 10^{10} ergs per second.

11. From the value of the ampere as defined on p. 12, and the atomic weight of silver, verify the number of coulombs required to deposit 1 gram equivalent.

12. A unit of work much used in electrochemical calculations is the volt-faraday (Mayer). What is the factor for converting calories into volt-faradays, and hence what is R in volt-faradays (see p. 11).

$$\text{Answer } \frac{1}{23070}$$

$$R = 0{\cdot}8606 \times 10^{-4}$$

1 calorie = 4·185 joules. 1 joule = $\frac{1}{96540}$ v. far.

$$1 \text{ calorie} = \frac{4{\cdot}185}{96540} = \frac{1}{23070} \text{ v. far. } \frac{1{\cdot}985}{23070} = 0{\cdot}8606 \times 10^{-4}.$$

THERMOCHEMISTRY.

For any change in a given system, the decrease of the intrinsic energy of the system (U) is equal to the external work done (A), minus the heat absorbed (Q).

$$A - Q = U \quad . \quad . \quad . \quad . \quad (1).$$ $\Delta E = Q - w$

(First law of Thermodynamics).

If a change from a state (1) to a state (2) is allowed to occur by two paths; and A, Q and A', Q' are the heat and work effects:

$$U = A - Q = A' - Q', \text{ etc.,}$$

because the change of the intrinsic energy (U) is independent of the path.

In many cases considered below the total external work effect (A) is small compared to the total external heat effect (Q). If the latter is divided into parts Q_1, Q_2, etc., corresponding to the separate reactions which together make up the whole change from state (1) to state (2), then :

$$Q_1 + Q_2 \cdot \;\cdot\;\cdot\;\cdot = Q'_1 + Q'_2 \cdot \;\cdot\;\cdot\;\cdot$$

Hess' Law.

Heats of Reaction at Constant Pressure and Constant Volume.

$$[\text{Reactants}] = [\text{Resultants}] + Q.$$

If reaction occurs at constant volume it is denoted by Q_v, or q.

If reaction occurs at constant pressure it is denoted by Q_p, or Q.

Molar equation of reaction :

$$n_1 A_1 + n_2 A_2 + \;\cdot\;\cdot\;\cdot \longrightarrow n'_1 A'_1 + n'_2 A'_2 \;\cdot\;\cdot\;\cdot$$

Neglecting the volumes of the solids, which is a justifiable approximation for ordinary pressures :

$$Q_p = Q_v + RT\,\Sigma n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where, in the summation Σn, all the n's (molar coefficients of gaseous reactants) are taken as positive, and all the n's (molar coefficients of gaseous resultants) are taken as negative.

Example $2\,H_2 + O_2$ (reactants) $\longrightarrow 2\,H_2O$ (resultants)

$$\Sigma n = 2 + 1 - 2 = 1,$$

and, therefore, in this case $Q_p = Q_v + RT$. RT = work done against constant pressure, by an expansion equal to the volume occupied by 1 mol. of perfect gas, at pressure p and temperature T.

Change of Heat of Reaction with Temperature.

$$\frac{dQ_v}{dt} = \Sigma n\,H_v\,{}^* \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where H_v = specific heat at that temperature (per mol.), at constant volume. (In the summation of H_v, the convention as to signs previously laid down is always retained).

---

* In this equation we can very approximately write H_p for H_v in the case of liquid or solid components.

If the specific heats do not vary with temperature, then :

$$[Q_v]_{t_2} - [Q_v]_{t_1} = (t_2 - t_1)\,\Sigma n\, H_v \quad . \quad . \quad . \quad (3)$$

$$\text{or } [Q_v]_{t_2} = [Q\ ]_{t_1} + (t_2 - t_1)\,\Sigma n\, H_v.$$

If the specific heats vary with temperature, the above equation still holds good; if H_v now denotes the mean specific heat per mol., at constant volume, over the temperature range t_1 to t_2 considered.

$$(\text{Mean specific heat between } t_1 \text{ and } t_2) \times (t_2 - t_1) = \int_{t_1}^{t_2} H\, dt,$$

where H is the true specific heat at temperature t.

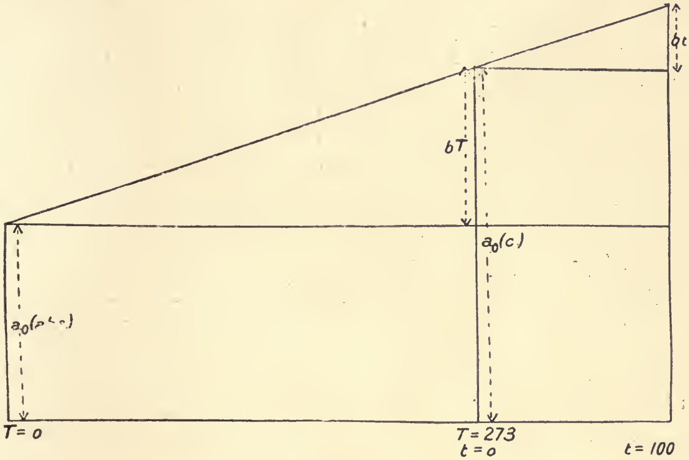


Fig. 1.

Alteration of Specific Heat with Temperature.

Suppose that H_v, the true specific heat per mol. at t, can be expressed as a linear function of the temperature, *i.e.*, $H_v = a + bt$, then $\Sigma n\, H_v = \Sigma n\, a + \Sigma n\, bt$ . . (4)

$$\frac{dQ_v}{dt} = \Sigma n\, a + \Sigma n\, bt \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$[Q_v]_{t_2} - [Q_v]_{t_1} = (t_2 - t_1)\,\Sigma n\, a + \tfrac{1}{2}\,(t_2^2 - t_1^2)\,\Sigma n\, b \quad . \quad (6)$$

Expressing temperature in absolute thermodynamic measure, and putting $H_v = a + bT$ (when, of course, a has now a different value), we can write also

$$[Q_v]_T = [Q_v]_0 + \Sigma n\, aT + \frac{\Sigma n\, b}{2} T^2 \quad . \quad . \quad (7)$$

Note that $[Q_p]_0 = [Q_v]_0$

Mean Specific Heats.

Suppose ${}_mH_v$ = mean specific heat per mol., at constant volume between 0° C. and t;

$$\text{then :—}{}_mH_v\, t = \int_0^t H_v\, dt = \int_0^t (a + bt)\, dt = at + \tfrac{1}{2} bt^2 \quad . \quad (8)$$

$$\therefore\ {}_mH_v = a + \tfrac{1}{2} bt = a + b't \quad . \quad . \quad . \quad . \quad (9)$$

$$\text{then } [Q_v]_{t_2} - [Q_v]_{t_1} = (t_2 - t_1)\, \Sigma n\, a + (t_2^2 - t_1^2)\, \Sigma n\, b' \quad (10)$$

Or, suppose ${}_mH_v$ = mean specific heat per mol., at constant volume, between absolute zero and T. Then, if H_v can be expressed as the linear function of T:

$$H_v = a + bT.$$

$${}_mH_v = a + \tfrac{1}{2} bT = a + b'T \quad . \quad . \quad . \quad (9\text{A})$$

$$\text{And } [Q_v]_T = [Q_v]_0 + \Sigma n\, aT + \Sigma n\, b'T^2 \quad . \quad . \quad (10\text{A})$$

It is to be noted that values of H_v given in the literature are usually *mean* specific heats, and not true specific heats, at any particular temperature.

For liquids and solids under ordinary pressures, we may put, as a sufficient approximation: $H_v = H_p$ where H_p = specific heat per mol., at constant pressures.*

For a perfect gas: $H_p = H_v + R$.

$$\text{Hence } \Sigma n\, H_p = \Sigma n\, H_v + R\, \Sigma n \, . \quad . \quad . \quad (11)$$

In this equation (see pp. 40, 147) the n's in the term Σn refer only to the molar coefficients of the gaseous reactants and resultants.

---

* Or, rather, in the previous equation we can write H_p for H_v in the case of liquids and solids in the presence of gases.

Combining now the equation:

$$\left.\begin{aligned} Q_p &= Q_v + RT\,\Sigma n \\ \Sigma n\, H_p &= \Sigma n\, H_v + R\,\Sigma n \\ \frac{dQ_v}{dt} &= \Sigma n\, H_v \end{aligned}\right\}\ \begin{array}{l}\text{In the term } \Sigma n \text{ only the} \\ \text{molar coefficients of} \\ \text{gaseous components} \\ \text{are employed.}\end{array}$$

We get: $\frac{dQ_p}{dt} = \Sigma n\, H_p$ . . . . (2A)

This equation can, of course, be deduced independently. We can treat it just as the former one, expressing now the specific heat per mol., under constant pressure as a linear function of the temperature.

$$H_p = a + bt \text{ or } {}_mH_p = a + b't.$$

In both cases the equations can be easily extended to the case where the specific heats vary more rapidly with the temperature, and have to be expressed as a more extended power series, *e.g.*,

$$h = a + bt + ct^2 \quad . \quad . \quad . \quad . \quad (12)$$

In the following formulæ and calculations dealing with the heats of homogeneous mixture and de-mixture (heats of solution, dilution, separation, etc.), any work effects due to changes of volume of liquids or solids are neglected, an approximation which is sufficiently exact at ordinary pressures.

PROBLEMS.

1. The heat of formation of Fe_2O_3 being 195,600 calories, and that of Al_2O_3 392,600 cal., what is the heat of the isothermal reduction of 1 mol. of Fe_2O_3 with Al?

Write out the equation according to the two usual methods.

Answer **197,000** calories.

$$\begin{array}{l} Fe_2 + O_3 = Fe_2O_3 + Q_1 \\ Al_2 + O_3 = Al_2O_3 + Q_2 \\ \hline Fe_2O_3 + 2Al = Al_2O_3 + 2Fe + Q_2 - Q_1 \\ Fe_2O_3 + 2Al = Al_2O_3 + 2Fe \\ -(Q_1) + (O) = -(Q_2) + (O) + (Q_2 - Q_1) \end{array}$$

Richards ("Metallurgical Calculations").

2. If the mixture 2 $NaOH$ *aq.* (dilute solution) with 2 HNO_3 *aq.* evolves 27,364 calories ; 2 $NaOH$ *aq.* with H_2SO_4 *aq.*, 31,378 calories ; and 2 $NaNO_3$ *aq.* with H_2SO_4 *aq.*, 576 calories, what is the thermal effect of mixing 2 HNO_3 *aq.* with Na_2SO_4 *aq.* ?

Calling the two acids A and A', and the base B—

$$A\ aq. + B\ aq. = AB\ aq. + Q_1,$$
$$AB\ aq. + A'\ aq. = ABA'\ aq. + Q_3$$
$$A'\ aq. + B\ aq. = A'B\,aq. + Q_2 \checkmark$$
$$A'B\ aq. + A\ aq. = ABA'\ aq. + Q_4$$

Answer $Q_4 =$ **3,438** calories absorbed.

Thomsen.

3. The heat of solution of 1 mol. of HI in dilute solution is + 19,207 calories ; the heat of vaporisation of solid I at 19° is — 5,448 calories ; the heat of formation of HI from $\frac{1}{2}$ H_2 and $\frac{1}{2}$ I_2 (solid) is — 6,036 calories ; find the heats of formation of HI from the gases at 19°—(1) gaseous ; (2) in dilute solution.

Answer (1) — **588** calories.
(2) + **18,619** ,,

Thomsen.

4. The heat of formation of H_2S (1 mol.) from H_2 and S (solid), is 2,730 calories. On solution in much water, a further 4,560 calories are evolved.

In the presence of water, $H_2S + 2\,I$ (solid) $= 2\,HI + S$ (solid).

In the absence of water, $2\ HI + S$ (solid) $= H_2S + I_2$ (solid).

From the data of the preceding problem, find the heat effect of these two reactions, taken from left to right.

Answer + **19,052** and + **14,802**.

Thomsen.

5. The heat of combustion of 1 mol. of rhombic sulphur to SO_2 (gas) at constant pressure is + 71,080 calories ; the heat of solution of SO_2 in much water is 7,700 calories. The heat of fusion of rhombic sulphur is 300 calories, and the heat of vaporisation of liquid SO_2 is 6,200 calories.

Find (1) the heat of formation of liquid SO_2 from liquid S and gaseous O_2;

(2) the heat of formation of dilute $SO_2\,aq.$ from liquid S and gaseous O_2.

Answer 71,080 + 6,200 + 300 = **77,580** calories.
71,080 + 7,700 + 300 = **79,080** ,,

Thomsen.

− 68,360 −78,630

6. $SO_2\,aq. + Cl_2 + H_2O = SO_3\,aq. + 2\,HCl\,aq. +$ 73,900 calories.

The heats of formation of 1 H_2O and 1 HCl (dilute solution) being 68,360 calories and 39,315 calories respectively, find the heat of the reactions:

$$(1)\quad SO_2 + \tfrac{1}{2}\,O_2 + aq. = SO_3\,aq.$$

$$(2)\quad SO_2\,aq. + \tfrac{1}{2}\,O_2 = SO_3\,aq.$$

(3) If the heat of solution of liquid SO_3 in much water is 39,170 calories, find the heat of formation of liquid SO_3 from liquid S and O_2.

Writing the equation in the abbreviated form adopted by Thomsen:

$$\begin{array}{l} SO_2\,aq. + Cl_2 + H_2O = SO_3\,aq. + 2\,HCl\,aq. \\ (-\,7{,}700)\qquad(-\,68{,}360)\qquad\quad(-\,78{,}630) + 73{,}900 \\ \qquad Q_1 + O + Q_2 = Q_x + Q_3 + Q, \end{array}$$

and $$Q_x = Q_1 + Q_2 - Q_3 - Q.$$

Where Q_1, etc., are the amounts of heat evolved in the decomposition of the various compounds, and Q is the net heat evolved by the whole reaction $= Q_1 + Q_2 - Q_3 - Q_x$.

Or, writing the energy equations in full, and adding:

$$\begin{aligned} SO_2\,aq. + Cl_2 + H_2O &= SO_3\,aq. + 2\,HCl\,aq. + 73{,}900 \\ SO_2 + aq. &= SO_2\,aq. + 7{,}700 \\ H_2 + \tfrac{1}{2}\,O_2 &= H_2O + 68{,}360 \\ \underline{2\,HCl\,aq. + 78{,}630} &\underline{{}= H_2 + Cl_2 + aq.} \\ SO_2 + \tfrac{1}{2}\,O_2 + aq. &= SO_3\,aq. + 71{,}330 \end{aligned}$$

The data of the preceding problem are required.

Answer (1) + **71,330** calories.
(2) + **63,630** ,,
(3) + **103,540** ,,

From the above data compare the heats of formation of liquid SO_2 and SO_3 from liquid S and gaseous O_2 at constant volume ($t^\circ = 17^\circ$ C.).

Answer **77,000** calories.
103,250 ,,

7. The isothermal "fusion" of Na_2SO_4 10 H_2O gives a liquid containing "a" of H_2O to 1 of Na_2SO_4, and a deposit of anhydrous Na_2SO_4. This partial fusion absorbs 16,509 calories per mol. of 10 hydrate disappearing, and $a = 15{\cdot}6$.

(1) What is the number of molecules of Na_2SO_4 in solution, and as solid, after 1 mol. of the 10 hydrate has disappeared?

(2) What is the heat evolved by the formation of Na_2SO_4 10 H_2O from Na_2SO_4 and saturated solution.

Consider 1 mol. of 10 hydrate. Let x mols. of Na_2SO_4 be transformed into solution, and therefore $(1 - x)$ of solid Na_2SO_4 precipitated.

$$H_2O = 15{\cdot}6\,x = 10 \therefore x = 0{\cdot}641.$$

One mol. of solid Na_2SO_4 is given by $\frac{1}{1 - x}$ 10 hydrate, and $\frac{1}{1 - x} = \frac{a}{a - 10}$.

Answer (1) **0·641** mols. in solution; **0·359** precipitated.
(2) + **46,000** calories.

8. From the heat of oxidation of SO_2 as stated in the preceding problems, combined with the following equation:

$$PbO_2 + H_2SO_3\,aq. = PbSO_4 + aq. + 76{,}700 \qquad (1)$$

find the heat of the reaction which takes place during the discharge of a lead accumulator (containing dilute acid), namely:

$$PbO_2 + Pb + 2H_2SO_4\,aq. = 2\,PbSO_4\,aq.$$

Determine $H_2SO_3\,aq. + \frac{1}{2}\,O_2$, etc. (as above) $+ Q_1$. (2)
Whence $Pb + O + H_2SO_4\,aq. = PbSO_4 + aq. + Q_2$ (3)
Subtract (1) from (2) and add (3).

Answer **86,800** calories.

9. What will be the heat effect, if acid containing 78 instead of 400 H_2O to 1 H_2SO_4 is used?

(See Problem 19, p. 31.)

2 $(Q_{400} - Q_{78})$ is to be subtracted.

Answer **85,700** calories.

10. The following figures refer to the heat of combustion of amorphous carbon at constant volume, the initial and final temperatures being 17° C.

$$C, O_2 = 96{,}960 \qquad 2\,CO, O_2 = 135{,}340.$$

Hence, find the heat of combustion of solid C to CO, at constant volume and constant pressure at 17°, and state a probable value for the heat of vaporisation of 12 grams of carbon, at 17°.

Answer + **29,290** calories at constant pressure.
29,000 calories at constant volume.
Q_{sv} for C at 17° = **38,380** calories.

Note.—This last result is obtained on the assumption that the formation of the double linkage $C = O$ evolves the same heat, whether the oxygen is attached to the same or different atoms.

$$C_S + O_2 = 2\,CO_2 + Q_1. \quad 2\,CO + O_2 = 2\,CO_2 + Q_2.$$
$$C_S = C_v + Q_{SV}.$$

11. If the heats of combustion of carbon and hydrogen, both at constant pressure and at 0° C. are:

$$H_2 + \tfrac{1}{2}\,O_2 = H_2O \text{ (vapour)} + 58{,}060$$
$$C + O_2 = 97{,}200 + CO_2$$

(1 gram) H_2O (vapour) $= H_2O$ (liquid) + 608 calories.
Also $C_2H_2 + 5O = 2\,CO_2 + H_2O + 315{,}700$ (water condensed).

$C_2H_6 + 7O = 2\ CO_2 + 3\ H_2O + 372{,}300$ (water condensed),

find the heats of formation of the hydro-carbons from solid C and H_2 at constant pressure and 0°.

Previously show that the volume changes by path (1) = those by path (2), and therefore no correction is required on account of change of volume.

$$C_2 + H_2 = C_2H_2 - \mathbf{52{,}300.}$$
$$C_2 + 3\ H_2 = C_2H_6 + \mathbf{29{,}100.}$$

Richards ("Metallurgical Calculations").

12. The combustion of 12 grams of carbon evolves 97,200 calories; that of 2 grams of H_2 evolves 58,060 calories to H_2O (vapour), and 69,000 calories to H_2O (liquid); all at room temperature, and constant pressure. The heat of formation of propane is + 33,850 calories. Hence, find the heat of combustion of propane at constant volume, and with condensed water at 15°.

1 vol. 5 vols. 3 vols. 4 vols.

$$C_3H_8 + 5O_2 = 3\ CO_2 + 4\ H_2O + (3 \times 97{,}200) + 4(69{,}000) + 2 \times 283.$$

Note.—The heat involved in the change of volume from steam to water is, of course, included in the difference 69,000 − 58,060.

Answer **534,326** calories.

13. The heat of formation of napthalene $C_{10}H_8$ (solid) being —19,450 calories, find the heat of combustion of the solid, without and with condensation of water.

Answer **1,223,690** calories per mol. without condensation.
1,267,450 calories ,, with ,,

Compare this with the value determined in the bomb with compressed oxygen.

(Problem 49, p. 42.)

14. The molecular heat of combustion of benzene (C_6H_6) to gaseous CO_2 and liquid H_2O, at constant pressure and 0° is given by Berthelot as 784,100 calories.

From the data of the last two problems, find the molecular heat of formation from C (solid) and H_2.

Answer **6,100** calories.

Richards (*loc. cit.*).

15. Taking the following round numbers for the heats of the following reactions, at 0° and constant pressure:

$$C + O_2 = CO_2 + 97{,}000 \quad . \quad . \quad . \quad (1)$$
$$CO + \tfrac{1}{2} O_2 = CO_2 + 68{,}000 \quad . \quad . \quad . \quad (2)$$
$$H_2 + \tfrac{1}{2} O_2 = H_2O + 59{,}000 \quad . \quad . \quad . \quad (3)$$

Find the heats of the reactions:

$C + \frac{1}{2} O_2 = CO$ (producer gas).
$C + 2\,H_2O = CO + 2\,H_2$.
$C + H_2O = CO + H_2$ (water gas).

Answer from (1) and (2) + **29,000** calories.
„ (1) „ (3) — **21,000** „
„ (1) (2) „ (3) — **30,000** „

16. It is required to make a water gas from air, steam and carbon, which shall contain no CO_2, and without heating or cooling of the producer. In what proportions, by volume must steam and air (both at 100° and same pressure) be blown in to bring about this result, allowing 10 per cent. loss, by radiation, etc., on all heat produced.

$$[C + \tfrac{1}{2} O_2 = CO + (29{,}000 - 2{,}900)]\, x$$
$$C + H_2O = CO + H_2 - 30{,}000.$$

Let x be number of gram atoms of carbon which must be burned, according to the producer gas equation (see last problem) to each gram atom burned, according to the water gas equation.

And x also represents the gram atoms of oxygen required for the combustion.

Answer **2·88** volumes of air to **1** volume of steam.

17. Expressing the weights of carbon and steam in kilograms, and quantities of heat in kilogram calories, the following are the thermochemical equations for the reactions in a gas producer.

$$\tfrac{1}{12}\,(C + O_2) = \tfrac{1}{12}\,(CO_2) + 8{,}100 \text{ Kal.}$$
$$\tfrac{1}{12}\,(C + \tfrac{1}{2}\,O_2) = \tfrac{1}{12}\,(CO) + 2{,}430 \text{ Kal.}$$
$$\tfrac{1}{18}\,(H_2O)\ (\text{steam}) = \tfrac{1}{18}\,(H_2 + \tfrac{1}{2}\,O_2) - 319 \text{ Kal.}$$

It is estimated that in a large producer, 10 per cent. of the total calorific value of the fuel is required to balance losses by radiation, etc. How much steam, therefore, can be decomposed by each kilogram of carbon burnt?

Answer **0·507** kilograms.

For the heat lost is 810 calories, and the total heat produced is 2,430 calories.

Richards ("Metallurgical Calculations").

18. Assuming all the conditions of the preceding problem, with the exception that 10 per cent. of the carbon is unavoidably burnt to CO_2. How much steam can be used for each kilogram of carbon, and what weight of air is required, in addition, to furnish enough O_2 for the combustion to CO and CO_2, in the proportions stated.

Answer **0·684** kilograms of steam.
3·859 ,, air.

The heat lost is the same as before; that produced is greater (0·1 kilo. burnt to CO_2 and 0·9 kilo. to CO).

The weight of air is calculated from that of the extra oxygen required to produce the CO and CO_2, taking the volume composition of air as 4 of N_2 to 1 of O_2.

Differential and Integral Heats of Solution.

(See Lehfeldt, "Physical Chemistry," p. 257.)

The heat effect observed on the mixture of one part of a substance A with x parts of B may generally be expressed as a function of x.

Thus, $q_x = f(x)$

The total heat effect thus obtained, *e.g.* in a calorimeter is called the integral heat of solution of so many mols. of B

in one of A. Thus, the heat evolved on mixing 10 mols. of H_2O with 1 mol. of H_2SO_4 may be written:

$$q_{10} = q \text{ (for } H_2SO_4 + x\ H_2O \text{ when } x = 10) = f(x)_{10}.$$

Heat of Dilute Solution.

A solution is dilute from this point of view, when further addition of x causes no further heat effect. The value of x has to be determined for each case.

Heat of Dilution (Integral).

If the original substance is already partly diluted, and $f(x)$ is known for the whole range of values of x, the heat of dilution between given limits is easily found.

Thus, for the heat of dilution of $H_2SO_4\ 10\ H_2O$ with 90 mols. more of H_2O:

$$q\ 10 \longrightarrow 100 = q_{100} - q_{10} = f(x)_{x=100} - f(x)_{x=10}.$$

Differential Heat of Solution.

The heat evolved per mol. of B on mixing B with infinite solution of composition: 1 of A to x of B. Or, in the language of differentials: if $x = 10$ $\left(\frac{dq}{dx}\right)_{x=10}$ is obtained by differentiating $f(x)$ with respect to x.

Heat of Dilution of Saturated Solution.

This is a special case in which x has a minimum possible value corresponding to the saturation concentration S.

Thus $\left(\frac{dq}{dx}\right)_{x=s}$ is the heat of dilution of a saturated solution, containing 1 of A to S of B.

The "last heat of solution" is another special case of the differential heat of solution.

The heat q_x evolved on mixing x of B (water) with 1 of A (salt) is known, say, as a function of x. From this, it is required to obtain the differential heat of addition of salt to water, when x corresponds to a saturated solution.

Dividing by x, $\frac{q_x}{x}$ is the heat produced by adding quantities $\frac{1}{x}$ of salt to 1 of water.

$$\frac{d\,\frac{q}{x}}{d\,\frac{1}{x}} = q + x^{-1} \times \left(- \frac{dq}{dx} \cdot x^2\right) = q - x \cdot \frac{dq}{dx}.$$

These relations are shown graphically in the diagram.

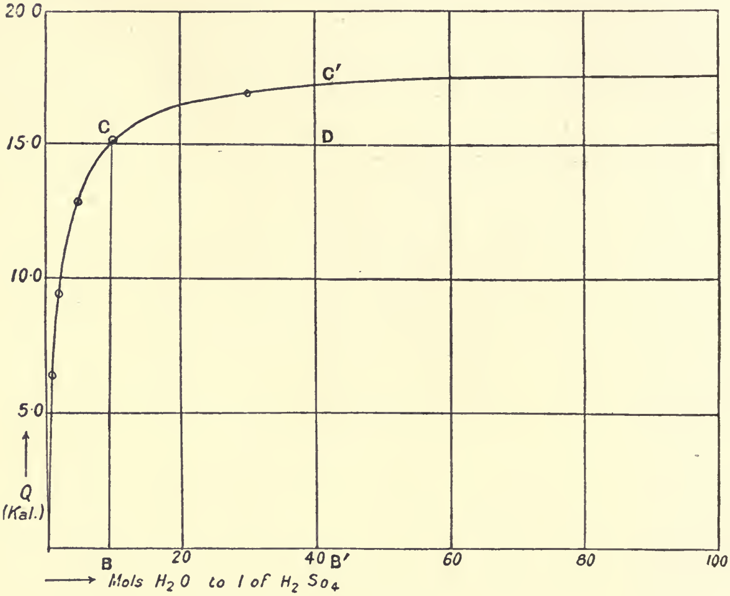


Fig. 2.

The curve will have somewhat the form shown, in which ordinates BC, $B'C'$ represent integral heats of solution; $C'D$ heat of dilution; the tangents at C and C' differential heats of solution at $x = B$ and $x = B'$.

The problems following may easily be solved by such a diagram.

19. The heat evolved on mixing A mols. of H_2SO_4 with B mols. of H_2O is given by the formula:

$$q = \frac{AB\ 17{,}860}{B + 1{\cdot}798\ A}\ \text{(Thomsen).}$$

What is the heat of mixing:

(1) 10 mols. of H_2SO_4 with 1 mol. of H_2O.
(2) 10 mols. of H_2O with 1 mol. of H_2SO_4.
(3) 1 mol. of H_2SO_4 with infinite water.
(4) 1 mol. of water with infinite H_2SO_4.

Answer (1) **15,130** calories.
(2) **9,480** „
(3) **17,860** „
(4) **9,931** „

20. On mixing acetaldehyde with ethyl alcohol, the following amounts of heat were evolved.

Plot the curve of q against per cent. of alcohol and aldehyde and find the heat evolved on mixing:

1 mol. of aldehyde with 1 of alcohol.
3 mols. of aldehyde with 2 of alcohol.

Mols. per cent. aldehyde.	q per mol. mixture.	Per cent.	q	Per cent.	q
81·10	+ 396·2	49·73	1,000·8	29·16	788·5
67·17	516·2	44·22	998·2	27·09	711·8
64·78	554·5	42·44	980·6	24·75	657·0
58·12	675·3	42·11	987·2	16·21	385·5
54·70	737·1	39·06	949·5	—	—
52·85	859·9	34·22	897·4	—	—
51·14	962·8	30·59	781·2	—	—

Answer (1) **1,940** calories.
(2) **3,205** „

Note.—The method of plotting the molecular percentage of A and B as abscissæ is apparent from the diagram of Problem 18, p. 30.

Smits (Proc. Roy. Acad. Science, Amsterdam, 1910).

21. In Problem 19, above, express A and B as fractional mols. per 1 total mol. mixture.

$$\text{Thus } \frac{B}{A+B} = \text{fractional mols. of } H_2O\ (a).$$

$$\frac{A}{A+B} = \text{fractional mols. of } H_2SO_4\ (1-a).$$

Plot $q_f = \frac{q}{A+B}$ (expressed in terms of a and the numerical constants) against the corresponding values of a. The "closed abscissa" method of plotting is similar to that employed in the last problem.

Hence, find the value of q_f, when 0·4 mols. of H_2O are mixed with 0·6 mols. of H_2SO_4. This may be done from graph.

Answer $q_f =$ **2,900.**

22. Two mols. of H_2SO_4 are added to, and 2 mols. of H_2O subtracted from a very large amount of acid, of composition $H_2SO_4 \,.\, 10\, H_2O$. This process is reversed in the case of acid of composition $H_2SO_4 \,.\, 3\, H_2O$. Using the preceding formula (Problem 19, p. 31), find the total heat effect of the two processes.

The heats in question are the differential $\frac{dq_B}{dx_B}$ and the negative of differential $-\frac{dq_A}{dx_A}$ for each concentration.

$$\frac{dq_A}{dx_A} = \frac{(B + 1{\cdot}8A)\, 17{,}860B - 17{,}860 \times 1{\cdot}8 \times AB}{(B + 1{\cdot}8A)^2}$$

$$= \frac{17{,}860B^2}{(B + 1{\cdot}8A)^2} \qquad \frac{dq_B}{dx_B} = \frac{17{,}860 \times 1{\cdot}8A^2}{(B + 1{\cdot}8A)^2}.$$

Answer **14,008** calories absorbed.

Dolezalek ("Lead Accumulator").

23. A solution of composition $CuCl_2 + 10\, H_20$ is diluted with $b - 10$ further mols. of water. The heat evolved in this dilution is given by the formula $q_b = \frac{b \times 5{,}023}{b + 21{\cdot}24}$ calories.

The heat of solution of $CuCl_2$ in 600 mols. of water is 11,080 calories.

Find the heat evolved on further dilution of $CuCl_2 + 600\ H_2O$ (the dilution being continued until there is no further heat effect); also the heat of solution of anhydrous $CuCl_2$ in 10 mols. of water.

(1) From the formula find:

$$q(_{10} \longrightarrow {}_\infty),\ q(_{10} \longrightarrow {}_{600})$$

hence $q(_{600} \longrightarrow {}_\infty) = $ **174** calories. Answer.

(2) $q(_0 \longrightarrow {}_{10}) = $ **6,231** calories. Answer.

Lehfeldt ("Physical Chemistry").

24. Two mols. of $NaNO_3$ dissolve in 10·9 mols. of water to form a saturated solution at 18°·0. Taking 2 mols. as the unit, the heat of solution in 12 mols. of water at this temperature is – 5,868, and the heat of dilution with x mols. is $-\dfrac{4{,}700\,(x - 12)}{x + 28{\cdot}96}$.

Find:—(1) The heat of solution in dilute solution from formula.

(2) The heat of solution of the dry salt in 10·9 mols. of H_2O.

(3) The heat of dilution of the saturated solution (*i.e.*, that evolved by the addition of 1 mol. of H_2O to a large quantity of the solution).

(4) The last heat of solution (1 mol. of salt in a large quantity of the saturated solution).

Answer (1) – **10,568** calories.
(2) – **5,738** „

(3) $\dfrac{d(f)x}{dx} = -\,4{,}700\dfrac{d}{dx}(x - 12)(x + 28{\cdot}96)^{-1} = -\,\mathbf{121{\cdot}2}$ calories.

(4) The formula connects q with the number of mols. x of b to 1 of a.

Change the variable so that the formula gives the heat evolution when $\frac{1}{x}$ of a is added to 1 of b (see p. 30).

Answer $- 5738 - (10{\cdot}9 \times - 121{\cdot}2) = - \mathbf{4{,}417}$ calories.

25. The mean molecular heat, at constant pressure of the permanent gases, at temperatures between 0°—200° C. has been found to be expressed by the formula :

$$H_p = 6{\cdot}8 + 0{\cdot}0_3 6t.$$

Taking R as $2{\cdot}0$, find a value for H_v at 0° C. and 0° absolute ; and a formula for finding the true molecular heats (H_v) at any temperature absolute.

$$H_v = H_p - R = 4{\cdot}8 + 0{\cdot}0_3 6t$$
$$H_v \text{ (at } 0°) = \mathbf{4{\cdot}8}. \quad \text{Answer.}$$

H_v (at 0° C.) $= a + 2\,b'T$ (b' being the coefficient of increase of mean molecular heat as above).

$$= H_v\,(0° \text{ abs.}) + 0{\cdot}0012T$$
$$H_v\,(0° \text{ abs.}) = 4{\cdot}8 - 0{\cdot}0012 \times 273 = \mathbf{4{\cdot}5}. \quad \text{Answer.}$$
$$\text{and } H_v\,(at\ T) = \mathbf{4{\cdot}5 + 0{\cdot}0012}T. \quad \text{Answer.}$$

26. Find the total quantity of heat given out when 28·08 grams of N_2 are cooled : (1) from 0° C. to 0° absolute ; (2) from 200° C. to 0° C.

$$Q\,(T \longrightarrow 0°) = aT + \tfrac{1}{2}\,bT^2 = aT + b'T^2$$
$$Q\,(t \longrightarrow 0°) = a_o t + b't^2.$$

Answer (1) $Q = \mathbf{1{,}275}$ calories.
(2) $Q = \mathbf{984}$ „

27. The true specific heats per 1 gram for CO_2 at constant pressure (Wiedemann) are :

0°	100°	200°
0·1952	0·2169	0·2387

Hence, find a formula for the alteration in the molecular heat of CO_2 from 0° to 200 (H_p) ; the mean molecular heat, at constant pressure, between 100° and 200° ; and the total heat given out on cooling 1 mol. from 200° to 0°.

Answer (1) $H_p = \mathbf{8{\cdot}6} + \mathbf{0{\cdot}00955}t$.

(2) $H_p\,(\text{mean})\,(100 - 200) = H_p(0) + \frac{1}{2}\,b(t_2 + t_1)$
$= \mathbf{7{\cdot}23}$ calories.

(3) $Q\,(200 \longrightarrow 0°) = H_p(0) + \frac{1}{2}\,b\,t^2 = \mathbf{1{,}911}$ cal.

28. The mean molecular heat at constant pressure $({}_mH_p)$ of water vapour at any temperature may be taken from the formula:

$$ {}_mH_p = 5{\cdot}8 + 0{\cdot}0029t, $$

Find ${}_mH_p$ between 100° and 200°; also the amount of heat given out by 1 mol. of water vapour in cooling from 200° to liquid water, at 0°, at constant pressure.

$\left\{ Q_{LV}\,(\text{at } 100°) = 537 \text{ calories per gram } h_p(\text{liquid from } 0° \longrightarrow 100°) = 1{\cdot}0. \right\}$

Answer (1) ${}_mH_p = \mathbf{6{\cdot}67}$ calories.
(2) **12,117** calories.

29. The mean molecular heat $({}_mH_v)$ of CO_2 has been expressed by the equation:

$$ {}_mH_v = 5{\cdot}106 + 0{\cdot}00334T - 7{\cdot}35 \times 10^{-7}T^2. $$

Hence, what is the true specific heat of CO_2 at 0° and constant pressure (H_p)?

$H_p = H_v + R,\ {}_mH_v = a + b't - c'T^2$

${}_oH_p = 2 + 5{\cdot}106 + 2 \times 0{\cdot}00334T - 3 \times 7{\cdot}35 \times 10^{-7}T^2$
$= \mathbf{8{\cdot}76}$ calories. Answer.

30. The specific heats of graphite and diamond at 0° or 17° are 0·1604 and 0·1128 calories per gram respectively. The heats of combustion are 94,810 and 94,310 per mol. of CO_2 formed at 17°.

Find the heat evolved in the transformation of graphite to diamond at 0° C.

$500 = q_0 + (h_g - h_d)\,\Delta t = q_0 + (0{\cdot}476 \times 17 \times 12)$

$q_0 = \mathbf{490}$ calories. Answer.

Note.—For such a small temperature interval the true specific heats are approximately equal to the mean specific heats.

Assuming a uniform decrease in the difference between the specific heats down to absolute zero, show that the difference between the mean specific heats 0° — 273° = $\frac{1}{2}$ $(h_g - h_d)$. (h_g = true specific heat, at 273°).

Hence, find the heat of transition at 0° absolute.

$$q_{273} - q_0 = (\Sigma n h_m)\ 273.$$

$$q_0 = \mathbf{412} \text{ calories. Answer.}$$

Weigert, Kohlenstoff (Abegg "Handbuch").

31. The mean specific heat of copper = 0·0939 + 0·0$_4$1778 t between 15° and its melting point.

Find the total heat which would be given out when 1 kilogram of melted copper is cooled from its melting point 1,085° to 15°. The heat of fusion (Q_{SL}) = 43 calories per gram.

Answer **161·5** Kalories.

32. Below 95°·4 C. rhombic sulphur S_r is stable with respect to the monoclinic form S_m. If the difference between the heats of solution for 1 gram $(Q_m - Q_r)$ is + 2·40 calories at 0°, and + 3·12 calories at 95°·4, and the mean specific heat ${}_m h_r$ of the rhombic variety per 1 gram, is 0·1769 over this range, find the mean specific heat of the unstable variety.

Let $Q_{m \longrightarrow r}$ = heat of transformation.

$$Q_{95} - Q_0 = ({}_m h_m - {}_m h_r) \times 95{\cdot}4.$$

$$\Sigma h_m = +\ 0{\cdot}0075.$$

Answer **0·1844** calories per degree.

33. The specific heats of ice and water being 1·0 and 0·5 respectively, and assumed constant over the range 0° . . . . — 9°, and the heat of fusion of 1 gram at atmospheric pressure being 80 calories, find the heat of fusion at — 9°.

Answer Q = **75·5** calories absorbed.

34. The quantities of heat given out in cooling from 1,300° to 0° by 1 kgm. mol. of ZnO, by 1 kgm. mol. of CO, and by 1 kgm. atom of C, are 17,075, 9,766, and 6,360 respectively.

The isothermal heats of combination of Zn, $\frac{1}{2}\,O_2$ and C, $\frac{1}{2}\,O_2$ are 84,800 and 29,160, at 0°.

Find (1) the heat of the reaction:

$$ZnO + C = Zn + CO \text{ at } 1{,}300°.$$

(2) The heat which must be supplied for each kgm. mol. of Zn produced, when the reactants are added cold, and the resultants taken from the furnace hot.

$$Q_t = \Sigma wh_m\,(t - t_0) - \Sigma wh'_m\,(t - t_0).$$

$Q_{1300} = -$ **80,166** calories. Answer (1).

And $Q_0 - h'_m t = -$ **103,601** calories. Answer (2).

Richards ("Metallurgical Calculations").

35. What is the more accurate value for Q_{1300}, taking into account the fact that while each separate reaction heat, as well as the total heat for the combined reactions is calculated for atmospheric pressure, the partial pressures of the Zn and CO formed are less than 1 atmosphere?

Answer $Q_{1300} = -103{,}601 + 3146 = -$ **100,455** calories.

Add the heat equivalent of work done by the external pressure in compressing Zn and CO each to 1 atmosphere.

Richards ("Metallurgical Calculations").

36. The heat of formation of CuO is 37,700 kilogram calories (Kal.) per kilogram molecule; that of Al_2O_3 is 392,600.

In the following, quantities of heat are expressed as kilogram calories (Kal.) per kilogram molecule; specific heats in Kal. per kilogram degree, etc.

The mean specific heat of Cu above its melting point (see Problem 31, p. 36), is taken as 0·1318.

The heat in solid Al_2O_3 to the melting point is estimated at 881·8 Kal., Q_{SL}, at 50·9, and the heat in liquid Al_2O_3 above 2,200°, at 0·5935 $(t - 2{,}200)$. Hence, calculate the temperature attained in this reduction.

$$3\,CuO + 2\,Al = Al_2O_3 + 3\,Cu.$$

The heat equation for Kal. and kgm. mols. is:

$95{,}135 + 60{\cdot}54\,(t - 2{,}200) + 3\,[10{,}303 + 8{\cdot}3825\,(t - 1{,}065)] = 279{,}500.$

Answer $t^\circ = \mathbf{3{,}670}$.

N.B.—Do not stand near this reaction, *Cu* boils at 2,100°.
Richards (" Metallurgical Calculations ").

37. Calculate the theoretical temperature obtained by the thermit reaction :

$2\,Al + Fe_2O_3 = Al_2O_3 + 2\,Fe$ (see Problem 1, p. 21), if the total heat in a kilogram of solid *Fe* at its melting point ($1{,}600^\circ \longrightarrow 0^\circ$) is 300 Kal., Q_{SL} is 69 Kal., and h_m (molten) is 0·25.

Answer $t = \mathbf{2{,}694}^\circ$

Heats of Reaction and Temperature.

38. If the mean specific heats per gram between 0° and 10° are as follows : $MgSO_4$ (anhydrous) $= 0{\cdot}225$; $H_2O = 1$; $MgSO_4 + 20\,H_2O$ (solution) $= 0{\cdot}744$, find the difference between the heats of solution of 1 mol. $MgSO_4$ at 10° and at 0°.

$Q_{10} - Q_0 = \Sigma w h_m\,(10^\circ \longrightarrow 0^\circ)$ where w are the weights of the reactants and resultants.

Answer $Q_{10} - Q_0 = \mathbf{300}$ calories.

39. If the mean specific heat of the hydrate $MgSO_4\,7\,H_2O$ is 0·406 (between 0° and 10°), find the difference between the heat effects when 1 mol. of $MgSO_4\,7\,H_2O$ is dissolved in 13 mols. of water at 0° and at 10°.

Answer $Q_{10} - Q_0 = -\,\mathbf{230}$ calories.

The heat of dilution of salt solution between given limits nearly always increases with the temperature. Show that this leads to the rule, that the specific heat of the weak solution, multiplied by its weight, is less than the sums of the specific heat of the strong solution and the added water, each multiplied by their weights.

40. The mean molecular heats of H_2, O_2 and H_2O are :

$$H_v = 4{\cdot}8 + 0{\cdot}0006\, t \ (H_2 \text{ and } O_2).$$
$$H_v = 5{\cdot}8 + 0{\cdot}0029\, t \ (H_2O).$$

If the heat of the combination of gaseous H_2 and O_2 to form gaseous H_2O, at constant volume and at 0° is:

$$H_2 + \tfrac{1}{2}\, O_2 = H_2O + 58{,}300 \text{ calories},$$

find a formula for the alteration of the heat of combination with temperature, and hence q at $t = 100$ and $t = 200$.

Answer $q - q_0 = \mathbf{1{\cdot}4}\ t - \mathbf{0{\cdot}002}\ t^2$
$q_{100} = \mathbf{58{,}420}$ calories.

41. From the preceding, find a formula for the alteration of Q_p with t from 0° to t° C., and the value of Q_p at 100° for each mol. of H_2O vapour and liquid formed.

$$_mH_p = H_v + R = a + R + bt.$$
$$\Sigma n\ H_p = \Sigma n\ H_v + \Sigma n\ R.$$

Answer (1) $Q - Q_0 = \mathbf{2{\cdot}4}\ t - \mathbf{0{\cdot}002}\ t^2$.
(2) $Q_{100} = \mathbf{58{,}793}$.

42. The mean specific heat of CO_2 from 0° to $t° = 0{\cdot}37 + 0{\cdot}0_3\, 22\, t$, and that of the gases N_2, O_2, H_2 and $CO = {\cdot}303 + 0{\cdot}0_4\, 27\, t$ (Kal. per cubic metre in each case). The heat of combustion of CO is 3,062 Kal. per cubic metre, and air consists of 3·808 volumes of N_2 to 1 of O_2.

Calculate the theoretical maximum temperature for the combustion of CO with the theoretical amount of air.

$$(0{\cdot}37 + 0{\cdot}577)\, t + (0{\cdot}0_3\, 22 + 0{\cdot}0_4\, 514)\, t^2 = 3{,}062.$$

Answer $t = \mathbf{2{,}050}$° C.

Richards ("Metallurgical Calculations").

43. The mean molecular heats of H_2, O_2 and H_2O from 100° C. downwards may be expressed by the formulæ :—

$$H_v = 4{\cdot}68 + 0{\cdot}0_3\, 26\ T\ (H_2, O_2).$$
$$H_v = 5{\cdot}62 + 0{\cdot}0_3\, 77\ T\, (H_2O).$$

If q at 100° = 57,650 for each mol. of H_2O formed, what will be the heat of reaction at absolute zero?

Answer $q_0 = \mathbf{114{,}400}$ calories for 2 H_2O.

44. The heat of formation of CO_2 from CO and $\frac{1}{2}$ O_2 at 273° being 68,000 calories, and the specific heats as follows:

$H_v = 5{\cdot}106 + 0{\cdot}00334\ T - 7{\cdot}35 \times 10^{-7}\ T^2)(CO_2).$

$H_v = 4{\cdot}68 + 0{\cdot}0_3\,268\ T\ (CO$ and $O_2).$

What is the heat of formation of 2 CO_2 at 0° absolute?

Also deduce a formula for the heat of reaction at any temperature, and find q at $T = 1{,}000$.

Answer $q_0 =$ **135,400.**

$$q = 135{,}400 + 3{\cdot}83\ T - 0{\cdot}0_2\,588\ T^2 + 1{\cdot}47 \times 10^{-6}\ T^3.$$

$q_{1000} =$ **146,580** calories.

45. It has been found by Le Chatelier that the molecular heats of gases (H_p) tend to a limit at the absolute zero.

$$H_0 = 3{\cdot}5 + 1{\cdot}5\ m.$$

(Where $m =$ the number of atoms in the gaseous molecule.)

Hence, find the value of $\Sigma n\ H_0$ for 2 H_2, O_2 and 2 H_2O_2 the specific heats of H_2 and O_2 being taken as positive.

Also prove, that for any gas reaction in which all reacting mols. are gases, the second term vanishes, since $\Sigma mn = O$.

Answer $\Sigma n\ H_0 =$ **3·5.**

General Formula for the Alteration of Gas Reaction Heats with T.

For a reaction between gases, as in the previous problem:

$$\Sigma n\ H_0 = \Sigma n\ 3{\cdot}5.$$

And the specific heat for each gas at any temperature T is given by the equation:

$$H_p = 3{\cdot}5 + 1{\cdot}5\ m + 2\ b'T.$$

$$\therefore \frac{dQ}{dt} = \Sigma n\ H_p = \Sigma n\ 3{\cdot}5 + \Sigma n\ 2\ b'T \quad . \qquad . \quad (1)$$

$$Q = Q_0 + \Sigma n\ 3{\cdot}5\ T + \Sigma n b' T^2.$$

For each molecular species in a condensed reaction:

$$H = a_0 + 2\ b'T,\ H_0 = a_0,$$

b'_s being the coefficient of increase of the mean specific heat of the condensed molecules.

$$\frac{d\,Q_s}{dt} = \Sigma n_s\,H_p = \Sigma n_s\,a_0 + \Sigma n_s\,2\,b'_s\,T \quad . \qquad (2)$$

the subscript s referring to the condensed molecules.

The term $\Sigma n_s\,a_0$ is equal to zero by Kopp's rule—*i.e.*, that the molecular heats of solid compounds at low temperatures are equal to the sum of the atomic heats of the constituent elements.

For a complete reaction, therefore, including gaseous and condensed molecules :—

$$\frac{dQ}{dt} = \Sigma n\,3{\cdot}5 + (\Sigma n\,2b' + \Sigma n_s\,2\,b'_s)\,T = \Sigma n\,H_p$$

$$+ \Sigma n_s\,H_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

$$\text{and } Q = Q_0 + \Sigma n\,3{\cdot}5\;T + \Sigma\,(n + n_s)b''\,T^2 \qquad (4)$$

the value $\Sigma(n + n_s)\,b''$ being derived from equation (3).

46. Given that Q for the reaction :

$$2\,H_2 + O_2 = 2\,H_2O$$

is 116,000 calories, at 373° absolute, and the molecular heats H_p at 450° absolute are :

$$6{\cdot}9\,(H_2),\ 6{\cdot}9\,(O_2),\ 8{\cdot}02\,(H_2O),$$

find the value of Q_0.

Answer **114,500** calories.

(See equation (1) above.)

Nernst (" Thermodynamics and Chemistry," p. 80).

47. Calculate the heat of the reaction :

$$H_2 + HgO = H_2O + Hg \text{ at } 0° \text{ absolute.}$$

Also find the formula for the variation of the reaction heat with temperature.

(See preceeding equations.)

$$H_2,\ \tfrac{1}{2}\,O_2 \longrightarrow H_2O \text{ (water)} + 68{,}200 \text{ calories.}$$

$$H_2O \text{ (water)} \longrightarrow H_2O \text{ (ice)} + 1{,}580 \text{ calories.}$$

$$Hg + \tfrac{1}{2}\,O_2 \longrightarrow HgO + 48{,}280 \text{ calories.}$$

All at 290° absolute. Values of H_p:

$$H_2 = 6{\cdot}8,\ HgO = 11{\cdot}2,\ H_2O = 9{\cdot}5,\ Hg = 6{\cdot}8.$$

Answer $Q_0 = \mathbf{47,520}$.

$$Q = \mathbf{47,520 + 3{\cdot}5}\ T - \mathbf{0{\cdot}003}\ T^2.$$

Note.—Find the correct value and sign of $\Sigma (n + n_s)\, b''$ from Equation (4), p. 41.

Nernst (" Sitz. Kon. Preuss. Akademie der Wissenschaften " (1909), 8, 258).

48. The following are the heats of combination, at constant volume, at 0°:

$$Fe_3 + 2\ O_2 = Fe_3O_4 + 270{,}800.$$
$$H_2 + \tfrac{1}{2}\ O_2 = H_2O + 58{,}060.$$

Find the heat of the reaction:

$$Fe_3O_4 + 4\ H_2 = 4\ H_2O + 3\ Fe,$$

begun and ended at 960° C., from the following data.

The total heat contained in 1 gram of iron between 0° and 960° is:

$$0{\cdot}218\ t - 39 \text{ calories.}$$

The specific heat of Fe_3O_4 in calories per gram is:

$$h_p = 0{\cdot}1447 + 0{\cdot}0_3\ 1878\ t.$$

The specific heats of H_2 and H_2O, calculated in calories per litre of gas, under standard condition $\left(\frac{1}{22{\cdot}22}\right)$ mols. are:

$$0{\cdot}303 + 0{\cdot}0_4\ 27\ t\ (H_2).$$
$$0{\cdot}34 + 0{\cdot}0_3\ 15\ t\ (H_2O).$$

$$\left.\begin{array}{l} Fe_3 + 2\ O_2 = Fe_3O_4 + 270{,}800 \\ H_2 + \tfrac{1}{2}\ O_2 = H_2O + 58{,}060 \end{array}\right\}\text{at } 0^\circ\ C.$$

Answer **— 7,961** calories.

Richards (" Metallurgical Calculations ").

49. One gram of naphthalene is burnt in a calorimetric bomb, which was immersed in 2,200 grams of water. The water value of the bomb, etc., was 480 grams. The rise of temperature, corrected for cooling was 3°·63. 0·025 grams of iron wire, with a combustion value of 1,600 calories per gram were used to initiate the combustion.

What is the heat of combustion of naphthalene?

Answer **9,688.**

Von Juptner (" Heat Energy and Fuels ").

50. The following data refer to a combustion by Krocker in the (Mahler) bomb calorimeter, of which the water value was 340 grams. The calorimeter contained 2,100 grams of water, and the rise of temperature, corrected for radiation, was $3^\circ{\cdot}002$.

0·0187 grams of iron were used, and the formation of H_2SO_4 and HNO_3 from this quantity of coal is estimated to absorb 8 calories.

The water was evaporated, and absorbed in $CaCl_2$ its weight being 0·48 gram.

Q_{LV} for gram of $H_2O = 600$ cal.

Find the lower thermal value of the coal (without condensation of steam).

$$\frac{(3{\cdot}002 \times 2440) - 29{\cdot}\,9 - 8}{1{\cdot}0772} = 6{,}764.$$

Answer $6{,}764 - {\cdot}48 \times 600 =$ **6,476** calories.

Von Juptner (" Heat Energy and Fuels ").

51. A bituminous coal is found to have the following composition in grams per 1,000: $C = 752$; $H = 52$; $O = 82$; $N = 10$.

Hygroscopic water = 34; ash = 70.

From the combustion values

$C, O_2 = 97{,}600$; $H_2, O = 69{,}000$ (liquid water),

$H_2, O = 58{,}200$ (steam),

find the combustion value of 1 kilogram of coal, in gram calories, available for steam raising. Also the volume-composition, and the total volume of the products of combustion with the theoretical quantity of air.

The total heat produced by the combustion of C and H_2, minus that required to vaporise the moisture gives the net calories produced; also the number of mols. of combustion products, and hence their volume at 0° and 760 mm. (1 mol. = 22·4 litres).

To this must be added the volume of nitrogen imported (*i.e.*, 4 times the theoretical volume of oxygen for complete combustion), in order to obtain the total volume of flue gas.

Answer **7,261** kilogram calories.

Total volume = **8·596** cubic metres composed of:
CO_2 **16·34** per cent.,
H_2O (uncondensed) **7·27**,
N_2 **76·39**.

Von Juptner (*loc. cit.*)

52. A certain coal has the following composition: $C = 69·83$; $H_2 = 4·33$; $N_2 = 0·50$; $O_2 = 12·38$; hygroscopic water = 7·25; ash = 5·71.

From this coal, gas was made in a producer.

The weight of ashes was 22·23 per cent. of the weight of the coal, and contained 68·76 per cent. of unburnt carbon.

The lower calorific value of the coal (moisture uncondensed) was 6,669 calories per gram.

The gas produced had the following composition by volume:

$$CO_2 = 5·21;\ CO = 23·99;\ O_2 = 0·63;\ CH_4 = 0·25;$$
$$H_2 = 10·64;\ N_2 = 59·28.$$

Find the cubic metres of gas produced from 1 kilogram of coal, and its calorific power in kilogram calories; and compare the calorific value of the gas with that of the coal.

One gram molecule of gas occupies 22·22 litres, and the calorific values in kilogram calories per cubic metre are as follows: $CO = 3{,}062$; $CH_4 = 8{,}598$; $H_2 = 2{,}620$.

The number of kilograms of carbon, gasified from 1 kilogram of coal may be obtained from the analysis of the ash.

The total carbon in 1 cubic metre of the gas is given by the amount of carbon-containing gases.

Thus, there is 0·0521 of a cubic metre of CO_2, and this contains:

$$\frac{1{,}000 \times 12}{22{\cdot}22 \times 1{,}000} \text{ kilograms of carbon.}$$

By summing up these quantities of carbon, and dividing into the quantity of available carbon in the coal, there is obtained the cubic metres of gas from 1 kilogram of coal. The calorific value of each constituent being known, the required comparison can then be made.

Answer Gas from 1 kilogram of coal
= **3·43** cubic metres.
Calorific power of gas
= **1,034·1** kilogram calories per cubic metre.
Calorific power of gas
= **53·2** per cent. of that of the coal from which it was obtained.

Richards ("Metallurgical Calculations").

SYSTEMS OF ONE COMPONENT.

The Gas Laws.

The gas laws are summarised in the equation:

$$pv = n\,RT \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

in which n is the number of gram molecules of gas, and R the universal gas constant.

(1) Boyle's Law.

$pv =$ constant (at constant temperature) or $d\,(pv) = pdv + vdp = 0$.

$$\left(\frac{dp}{dv}\right)_T = -\,\frac{p}{v}$$

(2) Gay Lussac's Law.

$v = v_0\,(1 + at)$ at constant pressure.
$p_t = p_0\,(1 + at)$ at constant volume.

$pv = p_0 v_0 (1 + at)$ at variable pressure and volume.

$$a = \frac{1}{273} \quad \therefore \text{ if } T = t + 273.$$

$$pv = p_0 v_0 \cdot \frac{T}{273}$$

(3) Avogadro's Hypothesis.

The relative weights of equal volumes (v_0) of different gases, at pressures (p_0) and equal temperatures ($T_0 = 273$) are found to bear simple relations to the combining weights as deduced from stoichiometrical relations.

If these relative weights, expressed in grams (*i.e.*, the gram-molecular weights) are taken as the units of weight, then, by definition $\frac{p_0 v_0}{273}$ has the same numerical value for all gases, and is called the universal gas constant R.

Note.—The molecular weights used in gas calculations are not, in general, those derived from the gas densities, but the more exact values, obtained by multiplying the atomic weights by the appropriate factors.

Second Law of Thermodynamics.

In the case of a gas expanding isothermally from a volume v_1 to a volume v_2:

$$A = \int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} RT \frac{dv}{v} = RT \log \frac{v_2}{v_1} . \qquad . \quad (2)$$

by equation (1), p. 45.

If a cycle of operations, consisting of two isothermal and two adiabatic parts (see p. 65) is performed upon a perfect gas, the work effect ΔA may be calculated from equation (2), as in Problem, p. 68.

If $Q + \Delta Q$, Q, are the amounts of heat absorbed at the higher temperature $T + \Delta T$, and rejected at the lower temperature T, during this or any other reversible process:

$$\frac{\Delta A}{Q} = \frac{\Delta Q}{Q} = \frac{\Delta T}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The maximum work ΔA is independent of the nature of the working substance employed in the reversible cycle.

Also the maximum efficiency:

$$\frac{\Delta Q}{Q + \Delta Q} = \frac{\Delta T}{T + \Delta T}$$

depends only upon the two temperatures.

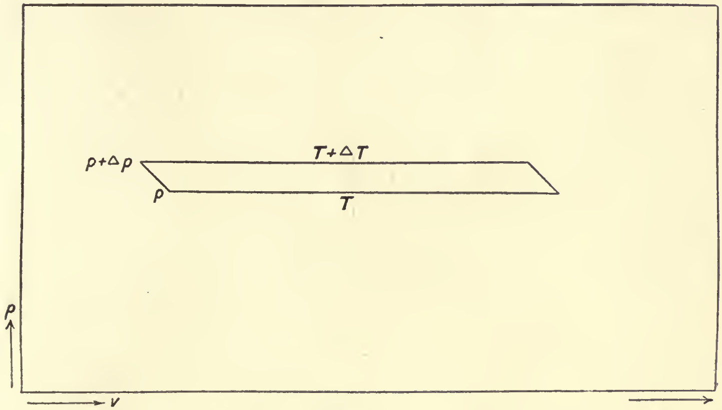


Fig. 3.

Combining equations (1) and (2) $\left(Q = T\frac{dA}{dT}\right)$ (see p. 17),

$$U = A - T\frac{dQ}{dT} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In many actual cases A, Q and U have finite values. The vaporisation of a liquid or solid may be taken as an example (see diagram).

Q = heat absorbed in the vaporisation of a stated mass (1 gram mol.), at constant pressure.

A = the external work done by the formation of vapour.

$U = q =$ the inner heat of vaporisation, or change of internal energy between the condensed and gaseous states.

Then, for isothermal vaporisation at constant pressure:

$$A = p(v_V - v_L) \qquad \frac{dA}{dT} = (v_V - v_L)\frac{dp}{dT}$$

$$T\frac{dA}{dt} = Q_{LV} = T(v_V - v_L)\frac{dp}{dT}$$

or $Q = T(v_V - v_L)\frac{dp}{dT}$ (Clapeyron's Equation) . (3)

The same equation may be used for any other change of state (*e.g.*, fusion) associated with a change of volume v_1 to v_2.

Thus, in the case of fusion:

$$Q_{SL} = T(v_L - v_S)\frac{dp}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3a)$$

where Q_{SL} is the latent heat of fusion at the melting point T, and $\frac{dT}{dp}$ is the rise in the melting point brought about by increase of pressure from p to $p + dp$.

If the vapour obeys the gas laws.

$v_V = \frac{RT}{p}$ (v_V being the volume of one gram molecule) and v_L is negligible compared to v_v.

$$Q = RT^2\frac{dp}{pdT} = RT^2\frac{d\log p \times 2{\cdot}3026}{dT} \quad . \quad . \quad . \qquad (4)$$

Clausius' Equation.

In practice, it is the integrated form of this equation which is usually required:

$$\int_{T_1}^{T_2} d\log p = \int_{T_1}^{T_2}\frac{QdT}{RT^2} \quad . \quad . \quad . \quad . \quad . \qquad (5a)$$

$$\left.\begin{aligned} \log p_2 - \log p_1 &= \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ Q &= \frac{RT_1T_2(\log p_2 - \log p_1)}{T_2 - T_1} \end{aligned}\right\} \quad . \quad . \quad . \qquad (5)$$

Or, substituting concentrations C for pressures p, and applying the relation:

$$p = CRT$$

$$\log C_2 - \log C_1 = \log p_2 - \log p_1 - \log T_2 + \log T_1$$

$$= \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \quad . \quad . \quad . \quad (6)$$

$+q$ being the inner heat of vaporisation, or the heat of vaporisation without the performance of external work. It is experimentally determined as the heat of vaporisation in a vacuum, or of condensation in a vessel of constant volume.

The same result may be obtained by substituting:

$Q = q + RT$ in the Equation (5a) and integrating.

Decisions as to the nature and direction of chemical changes are easily made with the assistance of the Le Chatelier, Van't Hoff principle of mobile equilibrium.

This principle can be universally applied.

For example: if the volume of the system consisting of liquid and vapour is slightly increased, the pressure would be decreased, were it not that more liquid evaporates, to restore the initial pressure.

The conversion of liquid into vapour takes place when the temperature is raised; consequently this is the process which is associated with the absorption of heat, and which tends to reduce the temperature.

Laws of Radiation.

Let E = the total energy emitted from a radiating body per second.

S = the surface of the body.

T = the time in seconds.

J = the intensity of the radiation.

T, T_0 = temperatures of the radiating and receiving bodies.

$$E = SKtT^4 \quad J = \frac{E}{St} = KT^4 \quad . \quad . \quad . \quad (1a)$$

Now, if E is the total energy, and J the intensity of energy received by a second body at temperature T_0,

$$J = K\,(T^4 - T_0^4) \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

These equations express the Stefan-Boltzmann Law, which applies to the perfect radiator, or black body. A coloured body will in all cases radiate less than a black one, at the same temperature.

The radiations from a black and coloured body are distinguished, in what follows, by the subscripts b and c.

The ratio of the amount of emission E, to the amount of absorption A, can be proved to be the same for all substances,

$$i.e.\ \frac{E_b}{A_b} = \frac{E_c}{A_c} \text{ (Kirchhoff's Law)} \quad . \quad . \quad . \qquad (2)$$

But a perfect black body absorbs all the radiation which falls upon it, *i.e*, $A_b = 1$.

$\therefore \quad E_c = E_b\,A_c$, A_c being less than 1.

Let λ be the wave-length (in $\mu = 0{\cdot}001$ mm.) of a particular radiation, and λ_m the wave-length of maximum energy radiation at any temperature,

then, $\lambda_m\,T = K_b = 2{,}940$ (black body) . (3)

$\lambda_m\,T = K_c$ (coloured body) . . . . (4)

Wien's displacement Law.

If E_m is the energy emission at wave-length λ_m

$E_m\,T^{-5} = B_b$ (black body) . . . . (5)

$E_m\,T^{-a} = B_c$ (coloured body) . . . . (6)

Stefan-Boltzmann Law.

The relation between J, λ and T has been worked out by Planck and Wien.

$$J = C_1\,\lambda^{-5}\left(e^{\frac{C_2}{\lambda T - 1}}\right)^{-1} \text{ (Planck).}$$

$$J = C_1\,\lambda^{-5}\,e^{-\frac{C_2}{\lambda T}} \text{ (Wien)} \quad . \quad . \quad . \quad . \qquad (7)$$

The simpler but less accurate Wien equation serves for most calculations.

The value of C_2 is about 14,500;

$\log e = 0{\cdot}4343$.

PROBLEMS.

The Gas Laws.

1. Calculate the constant $\frac{pv}{T}$ for 10 grams of H_2, O_2 and H_2O (steam).

At 0°, and 760 millimetres, 1 gram mol. of each gas occupies 22·40 litres.

Answer **0·410** litre atmosphere.
0·0256 „ „
0·0456 „ „

2. From the above constant, find the pressure exerted by 10 grams of steam when heated to 200° at constant volume, the original state of the system being defined by a temperature of 100° C., and a pressure of 1 atmosphere.

Answer p (at 200) = **1·27** atmospheres.

3. What is the volume throughout?

Answer v = **18** litres.
17

4. The relative density of $NOCl$ (air = 1) at 0° and 760 mm. is 2·31 (Tilden).

If 1 litre of air at 0° and 760 (N.T.P.) weighs 1·2931 grams, and 1 gram molecule occupies 22·4 litres, compare the theoretical molecular weight of $NOCl$ with that deduced from its density.

Answer **65·5** (theoretical).
66·9 (from density).

5. If a gram molecule of gas measured at 0° and 760 mm. occupies a volume of 22·4 litres, find the value of the universal gas constant R (1) in litre atmospheres; (2) in ergs.

For the answer, see Table, p. 11.

In calculating $\frac{pv}{T}$, the pressure and volume must be expressed in the appropriate units.

(For "p," see Problem 6, p. 16).

6. A cylinder of compressed oxygen, having a volume of 10 litres, contains so much oxygen as would occupy 1,200 litres at 1 atmosphere and 15°. It is used to charge a calorimeter bomb.

The volume of the bomb is 38 c.c., and the oxygen pressure required for a combustion is 25 atmospheres.

How many combustions can be carried out without refilling the cylinder?

Answer **100** combustions.

One litre of oxygen at 15° and 1 atmosphere may be chosen as the unit of quantity. Calculate the number of litres (measured as above) which must be left in the bomb in order that the pressure may be 25 atmospheres. The rest is available for combustion, and is to be divided by the volume of oxygen required to charge the calorimetric bomb to the required pressure.

$$p = \frac{n R T}{v} \qquad p_1 = \frac{n_1 R T}{v}.$$

7. Defining the concentrations, molecular normal and normal as one mol. and one equivalent per litre, find the molecular normality and normality of O_2 at atmospheric pressure and 0°, and also the pressure on the interior of a vessel filled with H_2, in normal concentration, at 0°.

Answer $C = \mathbf{0{\cdot}0447}$ and $\mathbf{0{\cdot}179}$

$p = \mathbf{11{\cdot}2}$ atmospheres.

8. The absolute density (grams per 1 c.c.) of a vapour at atmospheric pressure and a known temperature (above the boiling point of the liquid) may be determined by the method of Dumas.

By means of the gas laws, the absolute density which diisobutyl vapour (C_8H_{18}) would have at 0° and 760 millimetres, if no condensation occurred, is found to be 0·0051292.

The absolute density of H_2 under the same conditions is $0{\cdot}0_489873$ (grams per c.c.).

If the density of hydrogen is taken as 1, that of oxygen is 15·88.

Find the molecular weight of diisobutyl ($O = 16$).

Answer **114·144.**

$$M = \frac{D \times M_H \times 16{\cdot}00}{D_H \times 15{\cdot}88}.$$

M_H being the molecular weight of H, ($H = 1$) M, the molecular weight of the substance ($O = 16$) and D and D_H, the absolute densities.

9. Deduce a formula for calculating the theoretical absolute density of a gas, at any pressure and temperature, from a knowledge of the molecular weight ($O = 16$, and the absolute density of H_2.

Answer $$D_T = \frac{M \times D_H \times 15{\cdot}88 \times 273 \times P}{2 \times 16{\cdot}00 \times T \times 760}.$$

Find the absolute density of the saturated vapour of C_6H_5F, at 0°.

$P = 20{\cdot}92$ millimetres of mercury.

Answer $D = 0{\cdot}0_3 1179$.

10. The most generally useful method of determining vapour densities is that of Victor Meyer, in which a known weight of liquid vaporised at a temperature above its boiling point expels its own volume of air at the same temperature.

This air collected (often over water) at room temperature and pressure occupies the same volume that the weight of vapour taken would occupy, if it could be cooled to room temperature and normal pressure, without condensation.

In an experiment, 0·4068 grams of a volatile liquid displaced 45·3 cubic centimetres of air, measured at 15° and 740 millimetres, over water. The saturation pressure of aqueous vapour being 12·7 mm., and the density of $H_2 \times \frac{16}{15{\cdot}88}$ being $0{\cdot}0_4 9$ at N.T.P., find the molecular weight of the vaporised liquid ($O = 16$).

Answer $M = 110$.

11. What volume of air at (1) 80°·0, and (2) 100°·0, will be displaced from a Victor Meyer apparatus by 1 gram of benzene C_6H_6; and what volume will this air occupy (dry) at 0°. The pressure is normal throughout?

Use formula (1), Introduction, p. 45.

Answer **371·5** c.c. and **392·5** c.c.

At 0° and 760 mm. the air occupies **287·4** c.c.

12. Ethyl ether ($C_4H_{10}O$) is to be vaporised in a Victor Meyer apparatus at 100° C. and 760 mm.

The maximum capacity of the collecting tube for displaced air is 100 c.c.

The absolute density of H_2 at N.T.P. is $0{\cdot}0_49$.

What is the greatest weight of ether that can be used?

Answer **0·3156** gram.

13. Half a gram of ethyl ether, vaporised in a Hofmann apparatus, occupied 500 c.c. at 252·9 mm. If $M = 74$, find the temperature of the room.

Answer $t = 27°$ C.

14. The mean coefficient of increase of pressure at constant volume (α) is 0·003665 per degree, and the mean coefficient of increase of volume at constant pressure β is 0·003671 for air between 0° and 100°.

What are the absolute zeros (in degrees Centigrade) on the constant pressure and constant volume air thermometer? (See equations, Introduction, p. 45).

Answer − **272·8** and − **272·4**.

15. The deviation of a gas from Boyle's Law is given by the departure of the coefficient $\left(\frac{\delta v}{\delta p}\right)_T$ from unity, when p and v are both unity.

$$\text{Also } \left(\frac{\delta v}{\delta T}\right)_p = -\frac{\left(\frac{\delta p}{\delta T}\right)_v}{\left(\frac{\delta p}{\delta v}\right)_T}.$$

The coefficient α above for air at 4 atmospheres being 0·003708, and β being 0·003694, determine the deviation from Boyle's Law at this pressure.

(See equations, Introduction, p. 45.)

Answer $-\left(\frac{\delta v}{\delta p}\right)_T = \mathbf{0{\cdot}9938}.$

The gas is less compressible than if it obeyed Boyle's Law.

16. A constant volume thermometer containing gas enclosed by mercury (see Problem 18, below), and filled with helium to a fixed mark, at 0° and 100 mm., was heated to 100° C., the new pressure being 136·643.

When it was filled to the same mark with air, at 0° and 760 mm. and heated to 100°, the pressure became 1,038·99 mm.

Find the absolute zero as defined by *He* and air under the two pressures.

Answer Absolute zero = **− 272°·9** C. (*He*).
− 272°·4 C. (air).

17. If the pressures can be read accurately to 1 millimetre, what is the approximate accuracy of the temperature readings on the air thermometer, filled at 760 mm.?

Answer **0·1** of a degree.

18. As has been already seen, the temperatures ($\theta°$), defined by the expansion and pressure increase of the permanent gases agree closely with one another.

For thermometers with a variable mass of gas:

$$\frac{p_1 v_1}{pv} = \frac{n_1 R\theta}{nR\theta}.$$

If the quantity of gas remains constant:

$$\frac{v_1}{v} = \frac{\theta_1}{\theta} \text{ (at constant pressure),}$$

$$\frac{p_1}{p} = \frac{\theta_1}{\theta} \text{ (at constant volume).}$$

The temperature θ° as defined by a gas thermometer filled with a perfect gas must coincide with the absolute thermo-dynamic temperature T.

The temperature θ° as defined by such gases as O_2, N_2, He agrees very closely with T.

The work in gas thermometry carried out by Deville, Le Chatelier, Chappuis and co-workers will serve to illustrate the application of the gas laws.

The apparatus employed consisted essentially of a bulb in the heated area connected by a narrow bore tube (dead space) with a mercury manometer.

The temperature of the dead space and manometer necessarily rises during the experiment.

v = the volume of the thermometer bulb at room temperature (t_0).
β = the coefficient of expansion of the bulb.
h_0 and h_1 = the heights of the column of mercury at t°_0 and t°_1.
t_0 and t_1 = the initial and final temperatures of the dead space and manometric mercury.
D_0 and D_1 = the densities of mercury at t_0 and t_1.
T_0 and T = the absolute temperatures, initial and final of the heated bulb.
v_d = the volume of the dead space.
N = the total number of mols. of gas in the bulb and dead space.
n_0 and n_1 = the number of mols. of gas in the dead space, at the two temperatures t_0 and t_1.

Then, in the case of the constant volume thermometer:

$$\frac{pv}{p_0v_0} = \frac{h_1 D_1 v_0 \{1 + \beta (T - T_0)\}}{h_0 D_0 v_0} = \frac{(N - n_1)\, T}{(N - n_0)\, T_0} \quad . \quad (1)$$

$$\text{and } n_0 = \frac{p_0\, v_d}{R\,(t_0 + 273)} \qquad n = \frac{p\, v_d}{R\,(t_1 + 273)} \quad . \quad (2)$$

A porcelain bulb of 100 c.c. capacity to the beginning of the dead space (which consisted of 20 mm. of a capillary tube of 1 (mm.)^2 section) was filled with air at 760 mm. and 300° absolute.

When the bulb was heated in a furnace, the pressure registered on the manometer was 3,040 mm. and the temperature of manometer and dead space was, on the average, 350° absolute. If the coefficient of the cubic expansion of mercury is $0{\cdot}0_318$, and that of porcelain $0{\cdot}0_4135$, find the true temperature of the furnace.

Answer $T = \mathbf{1{,}209}°$ absolute.

First find an approximate uncorrected T from the change in p, neglecting the change in v and n; then the numbers of mols. of air (n_0 and n_1) in the dead space, at the two temperatures (300° and 350°), and finally the total number of mols. ($N = \frac{pv}{RT}$) present throughout the experiment (1 mol. occupies 22·4 litres at N.T.P.).

The values of $N - n_1$ and $N - n_2$, and v, the volume of the porcelain bulb at the approximate temperature calculated above may then be introduced into equation (1).

Le Chatelier, Boudouard ("High Temperature Measurements").

19. In the constant pressure gas thermometer, the vessel containing the gas is heated in such a way that the expanding gas can escape freely. The bulb is then closed, and the rise in temperature calculated from the amount of gas remaining in it.

If V and V_0 are the volumes of the thermometer, and n and n_0 the number of mols. of gas contained at the higher and lower temperatures, T and T_0:

$$\frac{pV}{pV_0} = \frac{n\,RT}{n_0 RT_0} \qquad n\,RT = \frac{V}{V_0 n_0} RT_0.$$

The difference between V and V_0 is small if the thermometer is made of porcelain or fused silica, and may be obtained with sufficient accuracy from an approximate calculation of the temperature.

A porcelain bulb containing initially 285 c.c. of air (v_1) at $T = 290^\circ$ and $p = 766\cdot4$ mm. was heated in the vapour of boiling cadmium. The bulb was then sealed. The volume of the contents measured afterwards at the initial temperature and pressure was 72 c.c. (v_2)

If the coefficient of expansion of the porcelain is $0\cdot0_4135$, what was the temperature of the boiling cadmium?

Answer $T =$ **1,164°.**

20. The experimental relation between pv and p for the same mass of gas at different pressures may be expressed by a power series: $pv = a + bp + cp^2$, etc.

The following values of pv were found by Wroblewski for the same mass of H_2.

t°	
$+\ 99\cdot14$	$pv = 1\cdot361299 + 0\cdot001360051p - 0\cdot0_54099268p^2$
0°	$pv = 0\cdot997393 + 0\cdot01308924p - 0\cdot0_54257472p^2$

Find the mean coefficient of volume expansion at the constant pressure of 1 atmosphere, between 0° and 100°.

Answer $\dfrac{v_1 - v_0}{v_0 \times t} =$ **0·003671.**

21. A closed manometer containing H_2 is used to measure high pressures.

A given volume v of H_2 at 0° and 760 mm. is found to be diminished to $0\cdot001\,v$, by a certain pressure.

Find the pressure.

$$pv = p_1 \times 0\cdot001v \quad \frac{p_1v_1}{pv} = \frac{a + bp_1 - cp_1^2}{a + b - c}.$$

Answer Pressure = **449** atmospheres.

Compare this with the pressure calculated on the assumption that pv remains constant.

22. The following are the corresponding values of p and pv for air, at room-temperature (Amagat):

p (mm.) =	760	5,000	30,000	60,000
pv =	1	0·99781	0·98551	0·98041

From the observed volumes of air in a closed manometer, on the assumption that Boyle's Law holds accurately, the pressures 5,000, etc., mm. were deduced. How many millimetres must be deducted in each case to obtain the true pressures?

Answer **11**, **441**, and **1,199** mm.

Velocity of Sound in Gases.

The elasticity of a gas is defined as

$$\frac{dp}{\frac{dv}{v}}, \text{ and } \frac{dp}{dv} = -\frac{p}{v} \text{ (Boyle's Law).}$$

Isothermal elasticity $= -p$.

Adiabatic elasticity $= -\gamma p \qquad \gamma = \frac{H_p}{H_v}$

The velocity of sound in a gas is given by the equation:

$$V = \sqrt{\frac{E}{D}},$$

where D is the density and E the adiabatic elasticity;

$$\text{therefore } V = \sqrt{\frac{\gamma p}{D}}.$$

23. Calculate the velocity of sound in air at 0° and 760 mm.

$$\gamma = 1{\cdot}40 \qquad D_{Hg} = 13{\cdot}6 \qquad D_{air} = 0{\cdot}001293$$

$$V = \sqrt{\frac{1{\cdot}4 \times 76 \times 13{\cdot}6 \times 981}{0{\cdot}001293}} = 33{,}130.$$

Answer **33,130** centimetres per second.

24. The velocity of sound in ammonia gas at 0° and 760 mm. is 41·5 metres per second.

If NH_3 has its theoretical density, calculate the ratio of the specific heats.

Answer $\gamma = \mathbf{1{\cdot}30}$.

If V is the velocity of sound in a gas, n the frequency or pitch of the sounded note and λ the wave length:

$$V = n\lambda.$$

The wave lengths λ_1 and λ_2 for different gases may be compared by means of a Kundt's tube filled with the gases, and containing a light powder which settles in heaps at the points where the air displacement is a minimum (half wave lengths).

If the densities D_1 and D_2, and also γ_2 are known, then γ_1 may be calculated, for the vibrating rod gives a note of the same frequency n throughout.

$$\frac{V_2}{V_1} = \frac{\lambda_2}{\lambda_1} \quad . \quad . \quad . \quad . \quad (1)$$

Introducing this into the equation of Problem 22,

$$\frac{\lambda_1}{\lambda_2} = \frac{\gamma_1 D_2}{\gamma_2 D_1} \quad . \quad . \quad . \quad . \quad (2)$$

25. A Kundt tube is filled successively with air and CO_2 at 15° and a pressure of 1 atmosphere.

The ratio $\dfrac{\lambda_{CO_2}}{\lambda_{air}}$ of the distances between the successive heaps of dust is 0·7766.

Find γ_1 for CO_2, if γ_2 for air is 1·41 and the density of CO_2 referred to air is 1·529.

Answer $\gamma_1 = \mathbf{1{\cdot}30}$.

26. If the velocity of sound in air under the above conditions is 339·58 metres per second, what is the velocity in CO_2?

Answer **263·7** metres per second.

(See equation (1), last problem.)

27. If the ratio γ is independent of temperature, what is the velocity of sound in air (1) at a pressure of 0·49 atmosphere, and 15° C.; and (2) at 1 atmosphere and 100° C.?

If v is the volume of 1 gram of gas, $D = \frac{1}{v}$ and $pv =$ constant $\times T$,

$\therefore$ At constant T, $D = \frac{p}{\text{constant}}$.

Also $\frac{p}{D} =$ constant $\times T$.

Answer (1) **339·58** metres per second.
(2) **396·9** „ „ „

28. If γ for air $= 1·406$ and $R = 1·985$ calories, find H_p for air and also the apparent molecular weight, if H_p for 1 gram is 0·239.

Answer $H_p =$ **6·8**.
$M =$ **28·8**.

(See previous problems, for the relations between γ, H_p, and H_v.)

Deviations from the Gas Laws.

The product pv for a constant mass of gas does not, in general, remain constant at constant temperature for different values of p.

The nature of the variation depends upon the nature of the gas and its temperature, and may be most easily grasped by plotting pv against p in some of the cases given below. A comparison may be made with the corresponding graph for a perfect gas, and that for a gas at a temperature below its critical temperature.

(See Young (" Stoichiometry ").)

The product pv may often be expressed with sufficient accuracy as a linear function of p, if p is less than 1 atmosphere.

Let p, v, p', v' be the pressures and volumes of equal masses of different gases, under standard conditions; and p_0, v_0, p'_0, v'_0 those of the same masses at zero pressure, and infinite volume.

It has been shown by D. Berthelot (" Sur les Thermomètres à Gaz ") that the true relative weights of the gas molecules are probably those derived from a consideration of $p_0 v_0$, since, under these conditions the deviations from the gas laws are at a minimum.

For each gas:

$$pv = p_0 v_0 \{1 - a(p - p_0)\}$$

$$\frac{v}{v'} = \frac{D'}{D} \qquad \frac{v_0}{v'_0} = \frac{D'_0}{D_0}$$

where D' and D'_0 are the absolute densities under normal and under limiting conditions.

If D is the density of the standard gas (H_2)

$$\frac{D'}{D} = \text{the relative density } d \ (H = 1).$$

$$\frac{pv}{pv'} = d \qquad \frac{p_0 v_0}{p_0 v'_0} = d_0;$$

$$\therefore \frac{do}{d} = \frac{pv'}{p_0 v_0'} \quad \frac{p_0 v_0}{pv};$$

$$\therefore d_0 = \frac{d\{1 - a'(p - p_0)\}}{1 - a(p - p_0)}.$$

29. The values of pv at 0° and 1 atmosphere, taken as unity in the case of H_2 and O_2 become, at 0° and 0·5 atmosphere 0·99974 (H_2) and 1·0038 (O_2).

Assuming that a remains uniform down to $p = 0$, find the relative density d_0 of oxygen at zero pressure, if d at N.T.P. is **15·90**.

Answer $d_0 =$ **15·88**

Young (" Stoichiometry " p. 18); Rayleigh (Phil. Trans. (1903), 204, 351).

30. One litre of hydrogen at a pressure of 2 atmospheres is expanded isothermally until it occupies two litres.

What is the new pressure?

Answer **0·9947** atmosphere.

31. The following are the values of a for the decrease of pv between $p = 1$ and $p = 6$ atmospheres. Assuming as before that a remains the same down to $p = o$, find the limiting molecular weights ($O_2 = 32$) of the following gases. from the relative densities ($O_2 = 1$ and $p = 1$).

	H_2	N_2	CO	O_2
$a =$	$-$ 0·00046	$+$ 0·00031	$+$ 0·00046	$+$ 0·00076
$d =$	0·062865	0·87508	0·87495	1·000

$$M = \frac{1\ a'\ (p - p_0)\} \times M(O_2) \times d\ (O = 1)}{1 - a\ (p - p_0)}\ .$$

Answer $M =$ **2·01472, 28·0132, 28·0068**, and **32·00.**

32. The temperature remaining constant at 0° C. throughout, a given weight w of a gas occupied v c.c., at $p = 1$ atmosphere. It is required to find the ideal density which the same gas would have if it strictly obeyed the gas laws. Let the volume which would be occupied at $p = 1$ atmosphere under these conditions be v_1 c.c. Assuming, as above, that the gas laws are strictly obeyed at zero pressure :

$$\text{then } p_0 v_0 = p v_1$$

If D_1 is the density corresponding to v_1 and D the absolute density observed :

$$\frac{D_1}{D} = \frac{pv}{pv_1} = \frac{pv}{p_0 v_0}\ .$$

The following values of pv and $p_0 v_0$ were found for O_2 by an extrapolation of the observed pressures, extending from 157 to 876 mm.

$p_0 v_0$	pv
139,769	139,628
139,087	138,959
56,311	56,256

Hence, calculate the mean value of a (see previous problems) and the ideal weight of a litre at N.T.P., if that actually found is 1·429 grams.

Answer $a =$ **−0·000964**
$D_1 =$ **1·42762.**

33. In the case of gaseous HCl, $pv = 54,803$ and p_0v_0 55213. The weight of a litre of HCl at N.T.P. being 1·63915, what is the molecular weight of HCl ($O_2 = 32$)?

Answer $M =$ **36·469.**

Gray and Burt (*Journ. Chem. Soc.* (1909), 95 II., 1633).

Second Law of Thermodynamics.

34. A perfect heat engine working between 200° and 300° absolute converts 20 calories into work. What is the actual amount of heat given out to the reservoir at 200° absolute? (see equation (2) p. 47).

Answer **40** calories.

35. How much heat would be converted into work by the same engine working between 200° and 100°, absorbing at 200° the same quantity of heat formerly absorbed at 300°?

Answer $\Delta Q =$ **30.**

$$\frac{Q + \Delta Q}{Q} = \frac{T + \Delta T}{T}$$

36. Defining the efficiency as the fraction transformed into work of the heat ($Q + \Delta Q$) absorbed at the higher temperature ($T + \Delta T$), calculate the efficiency of a reversible engine, working between 100° and 0° absolute.

Answer **100** per cent.

37. What are the theoretical maximum efficiencies of a steam engine (1) receiving steam at 140° C., and exhausting at 105° C.; (2) receiving at 250° C., and exhausting at 40° C.?

Answer (1) **8·47** per cent.
(2) **40·15** ,, ,,

38. Assuming the maximum efficiency for an ammonia refrigerator working between − 20° (expansion coils) and + 15° (compression coils), how many net kilogram metres of work must be done during the cycle in order to abstract 100 kilogram calories from the cooling (expansion) coils?

Answer **5,905** kilogram metres.

The refrigerator is to be considered as a reversed heat engine.

The work done by the gas during the expansion is imagined as being used to help in the compression.

Use equation (2), p. 46.

(See Table, p. 11).

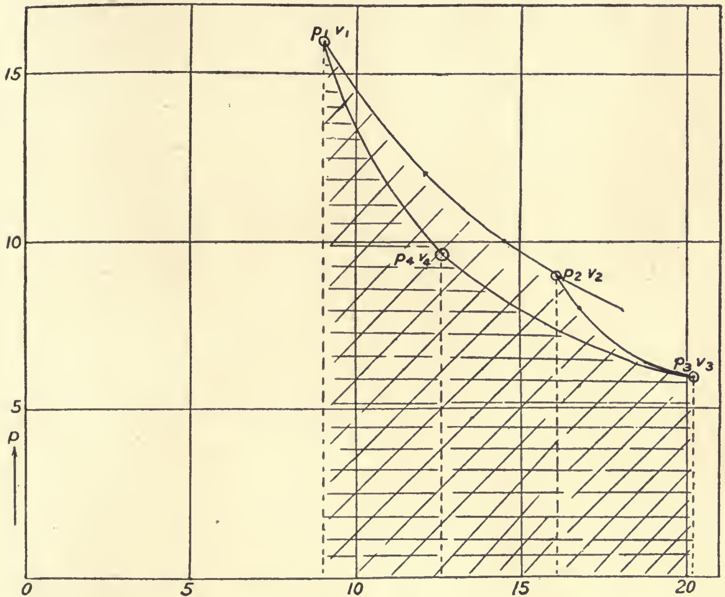


Fig. 4.

Isothermal and Adiabatic Changes.

The heat and work changes during a cycle of operations on any quantity of an actual gas may be calculated from a knowledge of the characteristic constants for the given quantity.

In the diagram, let p_1, v_1, p_2, v_2, etc., be the pressures and volumes at the corner 1, 2, 3, 4 of the quadrilateral, and T_1 and T_2 the temperatures of the (upper and lower) isothermals.

Let γ be the ratio of the specific heats $\frac{Hp}{Hv}\cdot$ It is required first to find the ratio of $\frac{v_3}{v_2}$ and $\frac{v_4}{v_1}\cdot$

For all points along the isothermals:

$$\left.\begin{aligned} p_1v_1 = p_2v_2 = RT_1 \\ p_3v_3 = p_4v_4 = RT_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the points along the adiabatics, it may be found that:

$$p_2v_2{}^{\gamma} = p_3v_3{}^{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combining equations (1) and (2)

$$\frac{p_2}{p_3} = \left(\frac{v_3}{v_2}\right) = \frac{RT_1v_3}{RT_2v_2}$$

$$\therefore \left(\frac{v_3}{v_2}\right)^{\gamma-1} = \frac{T_1}{T_2} \qquad \frac{v_3}{v_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}}. \quad . \quad . \quad (3)$$

$$\text{Similarly: } v_4 = v_1\left(\frac{T_1}{T_2}\right)^{1-\gamma}.$$

The amounts of work (which of course may be positive or negative) done by the gas between the states represented by points 1 and 2, 2 and 3, 3 and 4, 4 and 1 (and distinguished on the diagram by different kinds of shading) are numerically equal to the integrals $\int pdv$ (Introduction, p. 46). The value of this integral has already been obtained for the isothermal changes 1 ⟶ 2 and 3 ⟶ 4.

$$\int_{v_1}^{v_2} pdv = RT \ log \frac{v_2}{v_1}$$

In the case of the adiabatic changes 2 ⟶ 3 and 4 ⟶ 1 the integral of work done may be evaluated as follows:

From equation (2), if p, v are corresponding values at any moment:

$$p = \frac{p_2v_2{}^{\gamma}}{v^{\gamma}} \cdot \cdot$$

$$\text{and} \int_{v_2}^{v_3} pdv = p_2 v_2^{\gamma} \int_{v_2}^{v_3} \frac{dv}{v^{\gamma}}$$

$$= p_2 v_2^{\gamma} \cdot \frac{1}{1-\gamma} (v_3^{1-\gamma} - v_2^{1-\gamma}) \quad . \quad (4)$$

$$= \frac{p_2 v_2}{1-\gamma} [v_2^{-\gamma 1} (v_3^{1-\gamma} - v_2^{1-\gamma})]$$

$$= \frac{RT_1}{1-\gamma} \left(\frac{T_2}{T_1} - 1 \right) \text{ from (3)}$$

$$= \frac{R\Delta T}{1-\gamma} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The same result may be reached more simply,

Since $\Delta A - \Delta U = \Delta Q$, and the internal energy of a perfect gas is independent of its volume.

See Introduction,

$$\therefore \Delta U = O \qquad \Delta A = \Delta Q$$

The work done in this case is equivalent to the heat lost by the working gas.

But: $\Delta Q = - H_v \, \Delta T$

$$\therefore \quad \Delta A = \int_{v_2}^{v_3} pdv = - \frac{R\Delta T}{1-\gamma} \quad . \quad . \quad . \quad . \quad (5)$$

39. A quantity of oxygen originally at 0° C. is compressed adiabatically to one half its volume, then allowed to cool at constant pressure in a metal spiral in contact with water, at 17° C. and finally expanded adiabatically to one-third of its volume.

What are the temperatures immediately after the adiabatic compression and expansion?

Answer **360**° and **176**° absolute.

Use the adiabatic equation (3).

40. The numerical value of pv (litre atmosphere) for a certain mass of gas was found to be 144, and that of γ, 1·5.

The gas was expanded isothermally at 300° absolute, until the pressure fell from 16 to 9 atmospheres, then adiabatically, until the pressure fell to 6 atmospheres.

Supplement these results by means of the same intermediate values of pv and complete the cycle (diagram, p. 65). Also draw the v, t and p, t diagrams.

From the above data calculate (*a*) the number of mols. present; (*b*) the absolute temperature of the lower isothermal.

Answer (*a*) $N = \mathbf{5{\cdot}85}$.
(*b*) $T = \mathbf{253°}$.

41. One mol. of oxygen originally at 100° C. and occupying a volume of 11·2 litres is expanded isothermally to 22·4 litres, then adiabatically until the temperature falls to 50°. Finally it is compressed (1) isothermally, (2) adiabatically, until it reaches its first state.

Neglecting the slight inconstancy of pv and taking γ as 1·4, calculate the work and heat effects for each of the four parts of the cycle. Draw p, v and v, T diagrams of the process.

v_3 and v_4 must first be found, then the adiabatic work and heat from equations (4) or (5).

Answer A from (1) to (2) = **513** calories (work done and heat absorbed).
,, (3) to (4) = − **445** calories (work done and heat absorbed).
A from (2) to (3) = **250** calories (the same amount of heat is absorbed from the gas itself).
,, (4) to (1) = − **250** calories.

Properties of Liquids.

42. A certain pressure is found to be equal to that of a vertical column of mercury 800 mm. high as read against a glass scale (both at 10°). How many millimetres must be subtracted from this reading in order to obtain the true pressure expressed in millimetres of mercury, at 0°?

Answer **1·38** mm.

Each unit of height must be increased by *at* (*Hg*) and decreased by *at* (glass).

43. The following data refer to a dilatometer made of silica which has a coefficient of expansion, negligible compared to that of the contained liquid ($HgBr_2$).

Prideaux (Trans. Chem. Soc. (1910) 97, 2032).

Calibration with mercury at 16°·5.

The specific volume of *Hg* = 0·07375.

The weight of *Hg* to fill the bulb to the mark 1·10 on the stem = 29·0478.

The weight of the thread of *Hg* extending from 1·0 to 5·3 and 2·0 to 6·3, etc., on the stem = 1·2750.

The weight of $HgBr_2$ to mark 9·10 on the stem at 265° = 11·6833.

Find the molecular volume, or the volume of 1 gram molecule of $HgBr_2$, at 265°.

Answer **71·36**.

Surface Tension.

The surface tension of a liquid as defined below is that force which tends to decrease the surface of the liquid.

Its numerical value may be calculated from the height (h) to which the liquid rises in a capillary tube of radius r. If g = the gravity constant and d = the density of the liquid, then the surface tension $\gamma = \frac{1}{2} h r d g$.

If V = the molecular volume (see Problem 43, above), $V^{\frac{2}{3}}$ may be defined as the molecular surface.

The decrease of molecular surface tension with temperature is found to be linear, to within 6° of the critical temperature.

$$V^{\frac{2}{3}}\gamma . - V_1^{\frac{2}{3}}\gamma_1 = K(T_1 - T).$$

The equation must also express the fact that the surface tension vanishes:

$$\Delta^\circ\ (6^\circ) \text{ below } Tc$$

$$\therefore\ V^{\frac{2}{3}}\gamma = K\,(Tc - T - \Delta).$$

Young ("Stoichiometry," 348).

Eötvos (Wied. Ann. (1886), pp. 27, 448).

Ramsay and Shields (Phil. Trans. (1893), 184, 647); (Trans. Chem. Soc. (1893), 63, 1089).

44. In the case of benzene $t_c = 288^\circ{\cdot}5$ C.; $\Delta = 6^\circ{\cdot}5$; $K = 2{\cdot}1043$.

Find the value of the molecular surface tension $\gamma\, V^{\frac{2}{3}}$, at 100° and 200° C.

Answer **383·0, 172·5.**

45. The following results were obtained with carbon disulphide in a capillary tube of radius 0·0129 centimetres:

t°	d	h
19°·4	1·264	4·20
46°·1	1·223	2·80

Ramsay and Shields (*loc. cit.*).

If the acceleration of gravity is 980·6, find the value of the surface tension in dynes per square centimetre, at the two temperatures, and also the constant decrease of the molecular surface tension per 1°.

Answer **33·58** and **29·41** dynes per (cm.)^2.
$K =$ **2·022.**

46. The constancy of the decrease in the molecular surface tension for most non-associated liquids permits an approximate calculation of the degree of association of the liquid molecules.

Assuming the radius of any particular capillary tube to remain constant over the short range of temperature considered, show that:

$$\gamma\, V_M^{\frac{2}{3}} = (\text{constant})\ hd^{\frac{1}{3}}\, M^{\frac{2}{3}}$$

The constant is $\frac{1}{2}\,rg$.

In the case of formic acid ($HCOOH$), the increase in the molecular surface tension between 16°·1 and 46°·4 was found to be 0·902 per 1°, and between 46°·4 and 79°·8, 0·991 per 1°. If the mean constant for non-associated liquids is 2·121, find the mean degree of association of simple molecules $HCOOH$ over the two intervals of temperature.

Answer **3·61** and **3·13.**

Temperature Measurements.

If the property used to measure temperatures is approximately a linear function of the temperature as previously defined by some independent standard (*e.g.*, the expansion of mercury), the distance between two fixed points is divided into equal parts. This is done, for example, in the calibration of the ordinary mercurial thermometer.

If the property changes with the temperature in a manner which can best be expressed by means of a power series, the relations between the temperatures are most easily obtained from a calibration curve.

Thus, a platinum resistance thermometer has a resistance r_1 at 0°, r_2 at 50° C. and r_3 at 100° C.

Assume the r, t function to be linear at between 0° and 100° C.

$$\text{Then, } 0 = a + br_1.$$

$$100 = a + br_3.$$

$$b = \frac{100}{r_3 r_1} \text{ and } a = br_1.$$

Now 50° on this thermometer is actually equal to $a + br_2 + \Delta T$, the value of ΔT being given by the experimental value of r_2.

The whole series of intermediate ΔT are plotted against r, and the differences so obtained are added to the temperatures previously calculated from an observed r, by means of the linear formula deduced as above.

47. The following example is taken from Ostwald Luther ("Physiko-Chemische Messungen," Edition (3), p. 515).

t°	r
0	11·25
50	12·78
100	14·39
150	16·10
200	17·95

What are the constants of the linear formula derived from the above values at 0° and 200°, and what is the temperature which corresponds to a resistance of 15?

Answer $a = -$ **334·5.**
$b = +$ **29·85.**
$t^\circ =$ **118°·3.**

48. The variation in the electromotive force of a thermocouple with temperature is best expressed by a formula of the type:

$$\log E = a \log t + b$$

A certain thermocouple showed an E.M.F. of 3·265 millivolts in the vapour of boiling sulphur (445°), and one of 9·672 millivolts in melting copper free from oxide (1,085°). Find the numerical constants in the above formula if E is expressed in microvolts (0·001 of a millivolt).

$$3·9855 = 3·0355\,a + b \quad . \quad . \quad . \quad . \quad (1)$$
$$3·5139 = 2·6484\,a + b \quad . \quad . \quad . \quad . \quad (2)$$

Answer $a =$ **1·221** from (1) and (2)
$b =$ **2·776** from (2)

49. The formula for a certain platinum platinum-rhodium thermocouple is:

$$\log E \text{ (microvolts)} = 1·235 \log t + 0·241$$

if the cold junction is at 0°.

What is the mean value of each degree between 50° C. and 100° C., and between 700° and 750° (in millivolts)?

Answer **0·0056.**
0·0100.

50. Find a formula connecting the E.M.F. of this couple with the temperature on the Fahrenheit scale.

Answer $\log E = 1{\cdot}235 \log (t - 32) - 0{\cdot}074$

51. If the cold junction is not at 0°, the true temperature corresponding to any observed E.M.F. may be found by means of the Law of Successive Temperatures;

$$E\,(0^\circ - t^\circ) = E\,(0^\circ - t_1^\circ) + E\,(t_1^\circ - t^\circ),$$

where t_1° is intermediate between 0° and t°.

What number of millivolts must be added to the observed E.M.F. of the platinum platinum-rhodium couple mentioned above in order to obtain from the calibration curve the true temperature of a hot junction, if the cold junction is at 25° C.?

Answer **0·093** millivolts.

52. The intensity of the total radiation from a black body was found to be 23,190 calories, per (cm.)^2, at a temperature of 1,108° absolute (thermocouple); and 903·3 calories, at a temperature of 492°.

The bolometer receiving the radiation being in both cases at 290° absolute, find the constant K in formula (1), p. 50.

Answer **109·0.**

53. The radiation constant K of the Stefan Boltzmann equation (1a) is found to be:

$1{\cdot}71 \times 10^{-12}$ watts $= 0{\cdot}408 \times 10^{-12}$ calories per (cm.)^2, per second.

How many grams of water could be boiled away approximately per second by the radiation from 1 (cm.)^2 of a body at 6,000° absolute?

Answer **1** gram.

54. If the mean value of B_b is $2{,}188 \times 10^{17}$, find the temperatures of black bodies which give a maximum emission (E_m) of 13·66 and 14·50 (equation (5), p. 50).

Answer T = **910°·1** and **1,460°·0**

= **908°·5** and **1,460°·4** (observed).

55. At a temperature of 621°·2 the wave-length $\lambda_m = 4{\cdot}53\ \mu$; at $T = 1{,}094{\cdot}5$, $\lambda_m = 2{\cdot}71\ \mu$. Find the corresponding values of the constant in equation (5), p. 50.

Answer **2,814** and **2,966.**

56. What is the temperature corresponding to a wave-length of maximum energy $= 2{\cdot}35\ \mu$, if the mean value of the above constant is 2,940?

Answer $T =$ **1,250.**

57. Langley found the wave-length of maximum energy emission from the sun to be 0·0005 millimetres. What is the approximate temperature of the sun?

Answer $T =$ **5,880.**

58. The constant K $(= \lambda_m T)$ varies between the extreme values of 2,930 (for a black body) and 2,620 (for polished platinum).

The values of λ_m for the arc (carbon) light, Nernst glower, and Welsbach mantle are $0{\cdot}7\mu$, $1{\cdot}2\mu$ and $1{\cdot}4\mu$, respectively. Within what limits must the temperatures lie for each of these sources of light?

Answer $T =$ **3,700°—4,200°** absolute.
2,200°—2,450° ,,
1,875°—2,100° ,,

Waidner and Burgess ("Optical Pyrometry," Bulletin of the Bureau of Standards (Washington, U.S.A.), I. (1904—1905).

One class of radiation pyrometers is particularly suitable for illustrating the laws of radiation, namely, those in which the radiation of one particular wave-length in the visible spectrum is matched against a standard.

In the König spectrophotometer the lights from the incandescent source and from a comparison lamp are resolved into spectra by a prism inside the instrument. A comparison of the intensities at any desired wave-length may then be made by means of a rotating analyser.

The unknown and standard lights have been previously polarised, in planes at right angles to one another.

The Wanner technical pyrometer is the same in this respect, but the comparison at different wave-lengths is approximately attained by means of coloured glasses. The following description applies to both types of instrument.

To take a definite case,—all light from the comparison lamp is cut off when the analyser index is at 0°, and all light from the external source, when the index is at 90°.

If the fields have the same intensity of illumination when the analyser is at 45°, then $I_0 = I$, and if the angle of rotation required to produce the same illumination is ϕ, then $\frac{I}{I_0} = \tan^2\phi$.

Now, let the pyrometer be sighted successively on a black body at known temperature T, and on a source of unknown intensity which may be a coloured body, and let the angles read be ϕ_b and ϕ_c.

$$\frac{I_b}{I} = \frac{\tan^2{}_c\phi_b}{\tan^2\phi_c}$$

The Wien equation gives the intensity of radiation I_b of a black body, in terms of λ and T.

$$\text{Hence, } \log\frac{I_b}{I_c} = \log\frac{\tan^2\phi_b}{\tan^2\phi_c} = \frac{C_2 \log e}{\lambda}\left(\frac{1}{T_c} - \frac{1}{T_b}\right)$$

The temperature T_c of the unknown radiation may be determined from that of the known T_b.

The temperatures obtained from this equation by the use of the constant given on p. 50, are "apparent" or "black body" temperatures, *i.e.*, the temperatures which a black body would have, if it emitted light of the same intensity. It is, of course, the black body temperature of a standard source which is required in order to calibrate the comparison lamp. If the standard source happens to be black, a knowledge of its true temperature (*e.g.*, as given by a thermocouple) suffices for its calibration.

59. The percentage increase in $(f)\,x$ for a small finite increase in x may often be conveniently calculated from the differential (equation (1), p. 4).

Let $d\,x = \Delta\,x = 1$ (the unit of x).

Then, it is evident that:

$\dfrac{100(f')\,x}{(f)\,x}$ is the required percentage increase in $(f)\,x$.

Using the Stefan-Boltzmann equation (1), p. 50, calculate the percentage increase in intensity of radiation J, of a black body, per 1° rise of temperature:

(1) At 1,000° absolute; (2) at 2,000° absolute.

Answer (1) **0·4** per cent. per degree.
(2) **0·2** ,, ,, ,, ,,

60. What is the percentage increase per 1° at 1,000° absolute, in the selective radiation from a black body, at the wave-lengths:

$$\lambda = 0{\cdot}65\,\mu \text{ and } 0{\cdot}55\,\mu\,?$$

(See differential equations (2) and (1), p. 5, units).

Answer **2·2** per cent.
2·6 ,, ,,

61. A radiation pyrometer of the König type was calibrated by sighting on an incandescent object, of which the black body temperature was known to be 1,500° absolute.

The reading on the analyser scale was 50°·30′ and the wave-length employed was $\lambda = 0{\cdot}656\,\mu$. Find the black body temperature of the comparison lamp.

The constant C_2 of the Wien equation is taken as 14,500;

Answer $T =$ **1,485°**.

Use a table of logarithmic tangents.

62. The same pyrometer sighted on melted copper gave a reading of 48°·0′. When sighted on a black body at the same temperature the reading was 82°·45′.

Find the ratios between the intensities of the copper and the black body radiation at this temperature.

Answer $\frac{J_c}{J_b} = \mathbf{0{\cdot}157}$.

Burgess (Bulletin of the Bureau of Standards), 1909 (Oct.) VI., 1, 83).

63. If the thermocouple described in Problem 49, p. 72, read 10·19 millivolts just below the surface of the copper, what would be the black body temperature T_c of the copper?

Answer $T^{\circ} = \mathbf{1{,}253^{\circ}}$ absolute.

64. It is found that the intensities of light at $\lambda = 0{\cdot}64\mu$ for a black body at temperature T absolute are given by the equation:

$$\log J = 6{\cdot}697 - 9{,}983\frac{1}{T}.$$

Find the constants in the Wien equation.

Answer $C_1 = \mathbf{5{\cdot}346 \times 10^5}$.
$C_2 = \mathbf{14{,}700}$.

Burgess (Bulletin of the Bureau of Standards, 1904—1905, I., 218).

65. The results of the last problem were obtained by a Holborn Kurlbaum pyrometer, using coloured glasses. The same instrument was sighted on melted platinum (1,780° C.).

The intensity of the radiation was 5·662, when the wavelength chosen for the comparison was 0·55 μ.

What was the black body temperature of the platinum, and the ratio between the intensities of the radiation from the platinum and a perfect black body (at $\lambda = 0{\cdot}55\ \mu$)? Also, what is the ratio between the radiations from a black body at $\lambda = 0{\cdot}65\ \mu$, and $\lambda = 0{\cdot}55\ \mu$, the temperature being 1,780°?

Answer $t_b = \mathbf{1{,}577^{\circ}}$ C.

$$\left(\frac{J_{Pt}}{J_B}\right)_{\lambda = 0{\cdot}55\,\mu} = \mathbf{0{\cdot}24}$$

$$\frac{J_B\,(0{\cdot}65)}{J_B\,(0{\cdot}55)} = \mathbf{2{\cdot}9}.$$

One Component in Two Phases (Change of State).

The relation between vapour pressures and temperatures can be summarised by the formula of Biot:

$$\log p = a + b\,\alpha^t + c\beta^t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the calculation of these constants (which is somewhat lengthy) see Travers, Experim. Untersuch. Von Gasen, p. 261.

Ramsay and Young (Phil. Trans. (1886), 177, 123).

The differential $\frac{dp}{dt}$ may be calculated most accurately from this formula.

Show by differentiation that:

$$\frac{dp}{dt} = 5{\cdot}3019p\,(b \log \alpha\alpha^t + c \log \beta\beta^t) \quad . \quad . \quad (2)$$

When the vapour pressures of one liquid at various temperatures are known, the temperatures corresponding to the same pressures for another liquid may be deduced from the relation:

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + C\,(T'_A - T_A) \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + C'\,(T'_B - T_B) \quad . \quad . \quad . \quad . \quad (3)$$

Ramsay and Young.

Where T_A and T_B are the absolute temperatures corresponding to equal vapour pressures of A and B. The constant C is small, and may often be neglected, if the liquids are similar to one another.

66. The constants of the Biot vapour pressure formula in the case of diisopropyl $(C_3H_5)_2$ are:

$$a = 14{\cdot}002278$$
$$b = -\,10{\cdot}645849$$
$$c = -\,1{\cdot}699429$$

$$\log \alpha = \bar{1}{\cdot}999{,}792 \qquad \log \beta = \bar{1}{\cdot}995{,}33068$$

The formula is calculated from − 10° upwards, *i.e.*, 10 must be added to the temperature (° C.) before substitution in the formula.

Find the vapour pressure at:

$$t^\circ = 0^\circ,\ 100^\circ \text{ and } 170^\circ$$

Answer $p =$ **76·05, 2,409·7, 9,781** mm.

67. Correction of the boiling point to normal pressure $\frac{dt}{dp}$ can be determined for each pressure by the above formula, or more roughly from the vapour pressure, temperature graph.

Find the value of $\frac{dt}{dp{\cdot}T} = C$ for diisopropyl at $p = 760$ millimetres, and, hence the alteration of the boiling point for a decrease of pressure from 760 to 750 millimetres.

The values of p corresponding to $t^\circ = 40^\circ$, 50° and 60° may be found and plotted against t, then t° for $p = 760$ mm. is found from the graph.

Answer $C = \mathbf{0{\cdot}0_4828}$.

$$\Delta t = C \times T \times \Delta p = 0^\circ{\cdot}275.$$

Young ("Fractional Distillation," p. 15).

68. The value of C is 0·000145 for liquid oxygen, 0·00012 for most substances liquid at ordinary temperatures, and 0·0001 for water.

If the boiling points of O_2, C_6H_6 and H_2O are 90°·2, 353° and 373° respectively under a pressure of 760 millimetres, what will be the boiling points under 770 millimetres?

Answer **90°·13.**
353°·42.
373°·37.

69.

p mm.	T Methyl Acetate	T Propyl formate	T Ethyl acetate
20		271·95	269·8
100	282·05		299·35
760		353·9	350·1
2,000	360·9		383·05
4,000			411·25

Ramsay and Young (*Phil. Mag.* (1886), 21, 33); Young and Thomas (*Journ. Chem. Soc.* (1893), 63, 1258).

From the above data, calculate the constant C' in equation (3) above taking ethyl acetate as the standard liquid, and hence find the normal boiling point of methyl acetate, and the temperature at which propyl formate exerts a pressure of 4,000 millimetres.

Answer :—

C' for methyl acetate and ethyl acetate $= 0{\cdot}0_40$.
C' for propyl formate and ethyl acetate $= 0{\cdot}0_448$.
T_{760} (methyl acetate) $= 330°$.
T_{4000} (propyl formate) $= 416°{\cdot}6$.

Law of the rectilinear diameter (Cailletet and Mathias).

70. In the case of non-associated liquids the mean of the densities of the liquid and saturated vapour decreases linearly with the temperature.

Mathias (*Journ. de Physique* (1893), 11; (1892), 53); (Compt. Rend. (1886), 102, 1202; (1887), 104, 1563); Young (*Phil. Mag.* (1900), 50, 291).

Let D_t and D_o represent the densities of the liquid; Δ_t and Δ_o those of the vapour at temperatures $t°$ and $9°$ C., and D_c the critical density,

$$\frac{D_t}{2} = \frac{D_o}{2} + at \qquad \text{. . . . . . (4)}$$

$$D_c = \frac{D_o}{2} + at_c; \qquad \text{. . . . . . (4a)}$$

where t_c is the critical temperature and $t°$ and $0°$ are temperatures so low that the density of the vapour can be neglected in comparison with that of the liquid.

In the case of $SnCl_4$, $Do_{(273)} = 2{\cdot}279$, $D_c = 0{\cdot}742$ and $t_c = 319$.

Find a in the above formula, and hence calculate the density at the absolute zero, on the assumption that the law holds down to that temperature.

Answer $a = -0{\cdot}001243$

$$\tfrac{1}{2} Do_{(273)} = \tfrac{1}{2} D_{o(\text{abs.})} - a + 273a$$

$$D_{o(\text{abs.})} = 2{\cdot}958$$

71. The mean densities of pentane are connected as follows:

$$\frac{D + \Delta}{2} = \frac{D_o}{2} + at = 0{\cdot}3231 - 0{\cdot}00046t$$

At 150°, the density of the liquid is 0·4604, what is the density of the vapour?

And, if the critical temperature is 197°·2 C., what is the critical volume?

Answer (1) $0{\cdot}0_478$.

(2) 4·31 c.c. per gram.

72. Plot the following densities of liquid and gaseous oxygen (abscissæ) against temperatures (ordinates), and draw the diameter of the mean densities.

Hence, calculate the constants of the rectilinear diameter and the critical density, if $t = -118°{\cdot}8$ C.

t	D	Δ
− 210°·4	1·2746	0·0001
− 182°·0	1·1415	0·0051
− 154°·5	0·9758	0·0385
− 140°·2	0·8742	0·0805
− 129°·9	0·7781	0·1320
− 123°·3	0·6779	0·2022
− 120°·4	0·6032	0·2701

E. Mathias and H. Kammerlingh Onnes (Communications from the Physical Laboratory No. 117, The University Leiden).

Answer $\tfrac{1}{2}(D + \Delta) = 0{\cdot}1608 - 0{\cdot}002265t$.

$D_c = 0{\cdot}4299$.

Thermodynamics of Change of State.

73. The vapour pressure of water at 99°·5 is 746·52 millimetres; at 100°·5, 773·69 millimetres. The volume of

1 gram of saturated vapour at 100° is 1·658 litre. What is the value of Q_{LV} per gram, at 100° (in litre atmospheres), if D_{H_2O} (liquid) is taken as 1·0 at 100°?

Answer **22·065** litre atmospheres.

The value of $\frac{\Delta p}{\Delta t}$ may be obtained from the above data, and substituted for $\frac{dp}{dt}$ in equation (3) p. 48.

74. Show that the ratio of the energy required to do external work (A) to the total energy required for a vaporisation (Q) is equal to $\frac{p}{T\frac{dp}{dt}}$, and calculate the value of the ratio in the case of the last problem.

Answer **0·075.**

$A = p\,(v_V - v_L)$. Combine this with equation (3), p. 48.

75. p_1 for water at 273° = 4·54 millimetres and p_2 at 284°·5 = 10·02 millimetres.

Find Q_{LV} and q_{LV} for 1 mol. of H_2O at a mean temperature of 278°, assuming that the gas laws hold for aqueous vapour under these conditions.

$$\frac{d\log p}{dt} = \frac{Q}{RT^2} \qquad \frac{d\log c}{dt} = \frac{q}{RT^2}$$

Use the equations (5) and (6), pp. 48, 49.

Answer $Q =$ **10,550** calories absorbed.
$q =$ **10,050** ,, ,,

76. Q_{LV} for water, at 0° = 604 calories per gram.
Q_{SL} ,, ,, ,, ,, = 80 ,, ,,

The volume of 1 gram of saturated water vapour is 20,500 c.c., at 0°. Neglecting the volumes of ice and water, find the difference between the vapour pressures of ice and water at − 1° and + 1°.

$$\frac{\Delta p_{LV}}{\Delta t} = 0{\cdot}339 \text{ mm.} \qquad \frac{\Delta p_{SV}}{\Delta t} = 0{\cdot}384 \text{ mm.}$$

Answer: The pressure of water is greater than that of ice by **0·045** mm. at $-1°$; at $+1°$, that of the ice is greater by the same amount.

Nernst ("Theoretische Chemie").

77. The value of $\frac{\Delta p_{LV}}{\Delta t}$ for liquid benzene at its melting point, under atmospheric pressure (5°·6) is 1·905 millimetres per degree.

$$Q_{SL} = 30·18 \text{ calories for 1 gram.}$$

Assuming the gas laws to hold for the vapour, what is the value of $\frac{dp_{SV}}{dt}$ at the melting point $\left(\frac{\Delta p}{\Delta t}\right.$ is very nearly equal to $\left.\frac{dp}{dt}\right)$?

Use equation $\frac{dp}{pdt} = \frac{Q}{RT^2}$, and find the difference $\frac{dp_{SV}}{dt} - \frac{dp_{LV}}{dt}$ as above in terms of Q_{LV}, R and T.

$$\frac{dp_S}{p_s d_t} - \frac{dp_L}{p_L dt} = \frac{Q_{SL}}{RT^2}$$

$$\frac{dp_S}{dt} - \frac{dp_L}{dt} = \frac{Q_{SL}\,(p_S \text{ or } p_L)}{RT^2}$$

Q and R must of course be expressed in the same units.

Answer $\frac{dp_S}{dt} = \mathbf{2·446}$ mm. per 1°.

78. Solid benzene (0·4727 gram) in thermal contact with the ice of a Bunsen's calorimeter was distilled into a vacuum. The new ice formed in the calorimeter expelled 0·9954 gram of mercury.

Specific volume of ice at 0° = 1·090
,, ,, ,, water at 0° = 1·000
,, ,, ,, mercury at 0° = 0·07355
$Q_{SL} = 79·8$ calories absorbed (ice $\longrightarrow$ water at 0°).

What are the latent heats of evaporation (q_{SV} and Q_{SL}) of solid benzene?

Answer **136·7** calories per gram.
143·7 ,, ,, ,,

79. The latent heat of evaporation Q_{LV} of liquid benzene between 20° and 50° may be expressed as:

$$Q_{LV} = 107{\cdot}05 - 0{\cdot}158\,(t^\circ - 20).$$

Griffiths and Marshall (*Phil. Mag.* (1896) [5] 41, 1).

Assuming that this holds good down to 0°, calculate Q_{SL} at 0° from the above data and those of the last problem.

Answer $Q_{SL} = 143{\cdot}7 - 110{\cdot}2 =$ **33·5** calories per gram.

80. In the preceding examples the molecular weight of benzene vapour has been assumed to be 78. It can, of course, be found approximately from the vapour pressure curve which gives Q_M together with the experimental value of Q for 1 gram, since $\frac{Q_M}{Q} = M$.

The vapour pressure of liquid benzene at its melting point 5·4 is 36·0 mm. From the change of p with t (Problem 77, p. 83) and the value of Q_{LV} (Problem 79, above), find the molecular weight of benzene.

Use the approximate formula

$$\frac{\Delta \log p}{\Delta t} = \frac{Q_M}{RT^2}$$

Answer $M =$ **76·1**.

81. The vapour pressures of water and of ice at 0° are 4·6 and 4·6, and at − 9° are 2·33 and 2·08 mm. respectively (Ramsay and Young). What is the maximum work of transformation of 18 grams of water to ice at the two temperatures? Compare these with the heats of fusion (Thermochemistry, Problem 33, p. 36). See equation (2), p. 46.

$$A = 4{\cdot}57 \times 264 \times \log \frac{2{\cdot}33}{2{\cdot}08} = 59{\cdot}4$$

Answer **59·3** calories at − 9°.
0·0 ,, ,, 0°.

82. From the previous data, assuming that $\frac{dp}{dt}$ for solid and liquid benzene does not vary much over 10°, find the affinity of transformation (in calories) of 1 gram of the liquid to the solid, (1) at $-4^\circ{\cdot}6$, (2) at $+15^\circ{\cdot}4$

$$p \text{ at } 5^\circ{\cdot}4 = 36{\cdot}0 \qquad \frac{dp_L}{dt} = 1{\cdot}905$$

$$\frac{dp_S}{dt} = 2{\cdot}446$$

Answer $A_1 =$ **2·63** calories.
$A_2 =$ **− 0·69** ,,

83. It has been remarked that the value of $\frac{Q_{LV}}{T}$ is practically constant for all liquids which are not associated in the liquid or vapour condition (Trouton's Law), (where Q_{LV} = the latent heat of vaporisation of 1 mol., and T = the absolute temperature of vaporisation at a constant pressure). Find the constant for the following liquids:

Compound	Q per gram.	t° for a pressure of 760 mn.
C_6H_6	94·4	80°·2
C_5H_5N	101·4	117°·
H_2O	536·6	100°·
C_2H_5OH	216·5	78°·2
CH_3COOH	97·0	118°·5

Marshall and Ramsay (*Phil. Mag.* (1896) [v.] 41, 38).

Answer **20·65, 20·62, 25·64, 28·09, 14·89.**

N.B.—The molecular weight used in these calculations is the simplest formula weight, *e.g.*, CH_3COOH for acetic acid.

84. The average value of $\frac{Q}{T}$ being 21·0, find the latent heat of vaporisation per gram of a liquid with a molecular weight of 120, which boils at 200° C.

Answer **82·8** calories per gram.

85. If $\frac{Q}{T} = 20$, $R = 2$ and the vapour of a liquid obeys the gas laws at $p = 760$ mm., show that the rise of the boiling point due to an increase of pressure equal to 1 millimetre of mercury is approximately $\frac{T}{7{,}600}$ in the neighbourhood of the normal boiling point.

Roy. Coll. Sc. Ireland (Exam. 1909—1910).

86. The constant $\frac{Q}{T}$ varies with the temperature $\frac{Q}{T} = 9{\cdot}5 \log T - 0{\cdot}007T$ (Nernst).

Hence, find the increase of pressure (millimetres of mercury) required to cause a rise of 0°·1 in the normal boiling point at atmospheric pressure in the case of O_2 ($t_b = -182°$ C.) and HgI_2 ($t_b = +354°$ C.).

Answer dp for 0°·1 = **7·3** and **1·3** mm. respectively.

87. Find a general formula by means of which Q_{LV} may be calculated in ergs for any liquid of which the liquid and vapour densities are known, as well as the constants of the Biot vapour pressure formula (see Problem 66, p. 78).

$$Q = \frac{dp{\cdot}T(v_V - v_L)}{dt} = \frac{p}{(0{\cdot}434294)^2}\,(b \log \alpha\alpha^t + c \log \beta\beta^t)\,T\,(v_V - v_L).$$

The Biot formula expresses the vapour pressures in millimetres of mercury at 0°. If the density of Hg at 0° = 13·5956, $g = 980{\cdot}5966$ and 1 calorie = $4{\cdot}188 \times 10^{-7}$ ergs, a formula, with numerical constants connecting p (in millimetres) v_V, v_L in cubic centimetres per gram, a, β, b, c; t, T and Q (for 1 gram).

Answer :—

$$Q = \mathbf{168{\cdot}775}\,(b \log \alpha\alpha^t + c \log \beta\beta^t)\,\frac{p\,(v_V - v_L)\,T}{\mathbf{10^6}}$$

Mills (*Journ. Phys. Chemistry*, 8).
Young (“ Stoichiometry ”).

88. The pressures of diisopropyl at three temperatures have been calculated in Problem 66, p. 78. The liquid and vapour densities at these temperatures are as follows:

	$t = 0°$	$t = 100°$	$t = 170°$
$D_L =$	0·6795	0·5821	0·4885
$D_V =$	$0{\cdot}0_3384$	0·009901	0·04292

Find the corresponding values of Q_{LV}.

Answer **85·11.**
68·28.
49·36.

89. What is the external work in calories for the vaporisation of 1 gram of diisopropyl, (1) at 0°, (2) at 170° C., as calculated (a) from $p\ v$, (b) from $R\ T$, assuming that the gas laws hold for the vapour?

Answer (1) (*a*) **6·30** (*b*) **6·30.**
(2) (*a*) **6·61** (*b*) **10·2.**

The former of these values is, of course, the correct one at 170°.

90. It has been further shown by Mills (*Journ. Phys. Chemistry*) that on a theory of molecular attraction, a constant ratio should be found between the inner heat of vaporisation q, and the difference of the cube roots of the liquid and vapour densities. Calculate this ratio for diisopropyl C_6H_{14} at 0°, 100° and 170°.

Answer **97·81, 97·81,** and **97·71** $\left(\frac{q}{\sqrt[3]{D_L} - \sqrt[3]{D_V}}\right)$.

91. Effect of pressure on the transition temperature of condensed phases.

If V_1 and V_2 are the volumes of equal weights of the two phases (1) and (2), and Q the heat absorbed in the transition from (1) $\longrightarrow$ (2):

$$Q = T\frac{dp}{dt}(V_2 - V_1).$$

Compare equation (3a), p. 48. If V_2 is greater than V_1, then an increase of pressure will obviously raise the transition temperature, as in the case of the change liquid to vapour. The case of ice and water was studied by Lord Kelvin (1851).

The specific volume of ice at 0° is 1·091, and that of water 1·000. $Q_{SL} = 80$ calories absorbed.

By how much does an increase of pressure of 1 atmosphere alter the melting point of ice, and what is the melting point of ice under the pressure of its own vapour (4·6 millimetres at 0°)?

$$\frac{dt}{dp} = \frac{273(0{\cdot}001 - 0{\cdot}001091)}{80 \times 0{\cdot}0413} = -\,0^\circ{\cdot}0074. \quad \text{Answer.}$$

$$+\,\frac{0{\cdot}0074 \times 755{\cdot}4}{760} = +\,0^\circ 0073. \quad \text{Answer.}$$

92. The latent heat of fusion of paraffin wax at 52°·7 and 1 atmosphere being 35·35 calories per gram, and the increase of volume on melting being 0·125 c.c. per gram, find the melting point under a pressure of 10 atmospheres.

Answer **52°·97.**

Edser ("Heat," p. 372).

93. Below 95°·6 monoclinic sulphur (S_m) spontaneously changes into rhombic (S_r), while above this temperature the reverse change takes place. This is, therefore, the transition temperature.

By applying the principle of mobile equilibrium (see p. 49) decide whether heat is absorbed or evolved in the change $S_r \longrightarrow S_m$.

If the transition point is raised by 0°·0399 for each atmospheric increase of pressure, and the heat of transformation is 3·12 calories per gram, compare the specific volumes of S_r and S_m.

$$Q = \frac{T\,(V_m - V_r)}{1{,}000}\,\frac{dp}{dt}$$

Answer $V_m - V_r =$ **0·014** cubic centimetres.

Reicher.

MIXTURES.

Additive Relations.

Let S and S' be a specific property of two substances (refractivity, specific volume, etc.), and G and G' standard reference properties (mass or sometimes volume).

G and G' are additive properties, so that

$$G_M = G + G'.$$

(the subscript M refers to the mixture).

Now, if S and S' are also additive,

$$S_m (G + G') = SG + S'G'.$$

In some cases the volume may be taken as the standard additive property G.

Thus, the refractivity R_M of a mixture, containing V_1 and V_2 of two gases with the separate refractivities R_1 and R_2 (all volumes being, of course, measured under the same conditions) may be calculated by the formula :

$$R_M = \frac{R_1 V_1 + R_2 V_2}{V_1 + V_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Dilute Solutions.

Consider a dilute solution containing n mols. of a non-volatile solute, dissolved in N mols. of a solvent.

If one mol. of the liquid solvent occupies a volume of V litres, and if P is the osmotic pressure of the solute,

$$PV = CRT = \frac{n}{N} RT \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the constant R having the same numerical value as in the gas equation, p. 45.

By considering the isothermal transference of 1 mol. of the solvent from solvent to solution as vapour, and from solution to the solvent by an osmotic mechanism, it may be shown that the following relation holds (Van't Hoff):

$$RT \log \frac{p}{p_1} = \frac{n}{N} RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(p is the vapour pressure of the solvent, p_1 that of the solution).

$$\log \frac{p}{p_1} = \frac{p - p_1}{p_1} = \frac{n}{N} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(See p. 2.)

This equation allows the osmotic pressure to be calculated from the lowering of the vapour pressure.

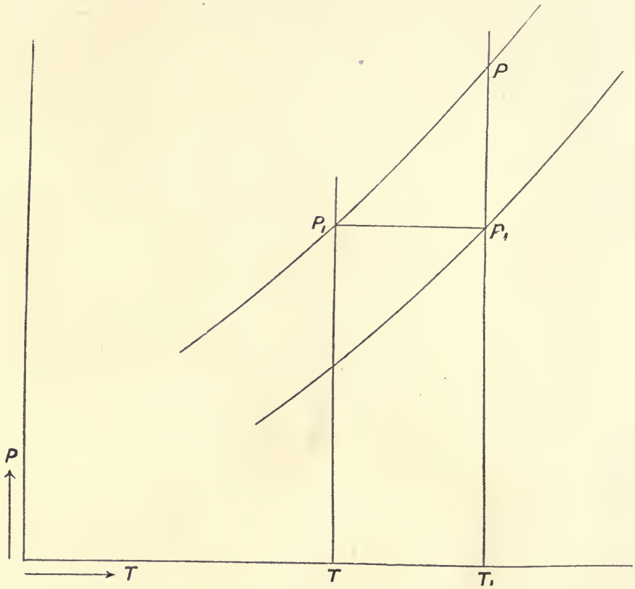


Fig. 5.

$$\text{For } PV = \frac{\Delta p}{p_1} RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

And V (c.c.) $= \dfrac{M}{D}$ (M = molecular weight of solvent). (D = density of the liquid solvent).

$$P = \frac{\Delta p \, D \, RT}{p_1 \, M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(R being expressed in appropriate units.)

In the case of dilute solutions Q_{LV} is the same for the evaporation of 1 mol. of solvent from the pure solvent or from the solution. (See diagram.)

$$\frac{d \log p}{dt} = \frac{d \log p_1}{dt} = \frac{Q}{RT^2} \quad \text{(see p. 48)},$$

or $\log \frac{p}{p_1}$ is independent of the temperature.

The heat of vaporisation Q_{LV} may be taken as constant over the range of temperature ΔT, between T the boiling point of the pure solvent, and T_1 that of the solution.

It then follows from equation (5), p. 48, that

$$\left.\begin{aligned} \frac{n}{N} &= \frac{Q_{LV}}{R} \cdot \frac{\Delta T}{TT_1} \\ \Delta T &= \frac{n}{N} \cdot \frac{RT^2}{Q_{LV}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

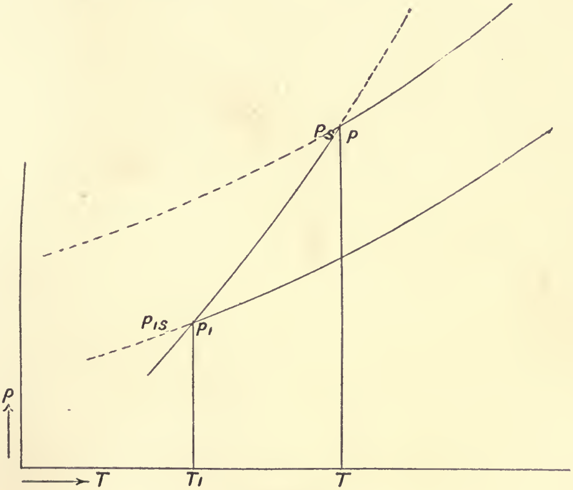


Fig. 6.

If T and T_1 be the freezing points of the pure solvent and the solution, and Q_{SL} be the heat of fusion of 1 mol. of the pure solvent, it may be similarly shown that

$$\log \frac{p}{p_1} = \frac{n}{N} = \frac{Q_{SL}\, \Delta T}{RTT_1} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\Delta T = \frac{RT^2\,n}{Q_{SL}\,N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Molecular elevation and depression

$$\frac{n}{N} = \frac{w\,M}{m\,W} \text{ (small letters refer to the solute).}$$

Let the gram molecular weight (as defined by Avogadro's Law) be dissolved in an arbitrary weight W (1,000 grams) of the solvent.

Then, since $\frac{Q}{M} = Q_1 =$ latent heat of change of state for 1 gram of solvent,

$$\Delta T_m = \frac{RT^2}{Q_1 \times 1{,}000} = \frac{0{\cdot}002 T_b^2}{Q_{1_{LV}}} \text{ (boiling)} \quad . \quad . \quad (9)$$

also $$\Delta T_m = \frac{0{\cdot}002 T_f^2}{Q_{1_{SL}}} \text{ (freezing)} \quad . \quad . \quad . \quad . \quad (10)$$

T_b and T_f being the boiling and freezing points of the pure solvent.

If the solvent exerts a vapour pressure, then by drawing the total pressure curves of the solvent and the solution, and the partial pressure curve of the solute, it may be shown that :

$$\left(\frac{n}{N}\right)_L = \left(\frac{n}{N}\right)_V + \frac{Q_{LV}\,\Delta T}{RT_1\,T} \quad . \quad . \quad . \quad . \quad (11)$$

L and V referring to the ratio of mols. solute to mols. solvent in the liquid and the vapour.

If the solute separates as a (dilute) solid solution with the solvent, then, applying the laws of solutions to the solid solution also :

$$\Delta T = \frac{RT\,T_1}{Q_{SL}} \left\{ \left(\frac{n}{N}\right)_L - \left(\frac{n}{N}\right)_S \right\} \quad . \quad . \quad . \quad (12)$$

One of the most important practical applications of these laws is the determination of the molecular weight of the solute or solvent.

Thus, for a weight w of solute of molecular weight m, dissolved in W grams of solvent of molecular weight M:

$$\Delta T = \left(\frac{RT^2}{Q_1 W}\right)\frac{w}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The quantity enclosed in brackets is a constant for a fixed amount (100 or 1,000 grams, or c.c.) of the solvent, and may be determined once for all, either from Q and T for the pure solvent, or a freezing or boiling point determination with a solute of known molecular weight.

Then if ΔT refers to a substance of unknown molecular weight m,

$$\frac{\Delta T}{\Delta T_m} = \frac{w}{m} \qquad m = w\,\frac{\Delta T_m}{\Delta T} \quad . \quad . \quad . \quad . \quad (14)$$

w being the weight of the solute dissolved in the arbitrary weight or volume of the solvent.

The following are some constants for the elevation of the boiling point, or the depression of the freezing point, when 1 gram molecule of a solute is dissolved in a kilogram of the specified solvent.

Solvent	t_f	Δt_f	t_b	Δt_b
Water . . .	0°	1·86°	100°	0·519°
Benzene. . .	5·4	5	80	2·70
Naphthalene . .	80	6·9		
Phenol . . .	41	7·3	132	3·04
Nitrobenzene .	55	7·0	207	5·02
Ethylene bromide .	8	12·0	132	6·43
Ethyl ether . .			35	2·10
Chloroform . .			61	3·60
Acetic Acid . .	17	3·9	118	3·00
Ethyl Alcohol .			78	1·17
Acetone . . .			56	1·70
Ethyl Acetate .			75	2·70

Phase Rule.

The relations between the pressure, temperature, and concentration of mixtures can be represented by plane P, T and C, T diagrams sufficiently well for many practical purposes.

The phase rule theoretically deduced by Willard Gibbs forms the most important guide in constructing and interpreting these diagrams.

Components. Let m be the number of components or constituents independently variable under the given conditions.

Thus Na_2SO_4 and water is a system of two components.

Na_2SO_4, $CaCl_2$, $CaSO_4$, $NaCl$ (reciprocal salt pair) and water constitute a four-component system, since, given the concentration of three salts (or ions) that of the fourth is determined by the stoichiometrical laws (law of electrical neutrality).

Phases. Let r be the number of phases. A gas or mixture of gases forms one phase. A pure liquid, solution, or mixture of liquids forms one phase. Each pure solid forms a separate phase, but if there is reason to expect the presence of a solid solution (see Problem 26, p. 107) then the two solids mutually dissolved constitute only one phase.

Thus $CaCO_3$, CaO and CO_2 form three phases, two solids and a gas (two components).

In the absence of vapour the system I in C_6H_6 (liquid and solid solutions) consists of two phases (two components). But a "cryohydrate" $NaCl\ 2\ H_2O$, ice and solution consists of three phases (two components).

Degrees of Freedom. Let f be the number of degrees of freedom, or factors (pressure, temperature and concentration of each component) controlling the system, which can be altered at will, without causing an alteration in the number of phases (appearance or disappearance of a phase).

Thus p and t are the factors controlling the state of the system, water, liquid and vapour. The temperature can be raised, but if it is attempted to vary the pressure at a fixed temperature, either the liquid or the vapour phase disappears, *i.e.*, the system has one degree of freedom.

The number of phases, etc., consistent with equilibrium is given by the equation:

$$f = n - r + 2 \quad . \quad . \quad . \quad . \quad (1)$$

Absence of Vapour Phase. A system in open vessels is not usually in true equilibrium, since it tends to lose vapour continually to the surrounding air. In the case of the most important aqueous systems the partial pressure of aqueous vapour is seldom equal to that of the air, as is sufficiently brought home to every chemist by the facts of deliquescence and efflorescence of hydrates, or the drying up of solutions. Frequently, however, the disturbance of equilibrium due to gain or loss of vapour is slight, and the phase rule may be effectively applied to such open systems, the number of phases r, and degrees of freedom f being each diminished by one.

Thus the system $NaCl$, H_2O in phases $NaCl$ solid, solution and vapour is univariant (one degree of freedom) in a closed vessel,

Since: $f = 2 - 3 + 2$.

It is also univariant when exposed to the air, if we ignore the small readjustments due to loss of vapour,

Since: $(f - 1) = (2 - 2 + 2) - 1$.

Thermodynamics of Mixtures.

The phase rule is not a complete guide to the changes which take place in heterogenous systems, but must be supplemented by other deductions from the laws of thermodynamics.

From the Le Chatelier, Van't Hoff principle of mobile equilibrium already stated for one-component systems, it is evident that if the act of solution is associated with absorption of heat, solution will take place on the addition of heat. Further, it appears from the Clausius equation that the solubility will increase with the rise in temperature.

If at any temperature there are two condensed substances *A* and *B*, which can pass into one another (such as dimorphous or other allotropic forms, polymers, isomers), then, if *A* has the greater vapour pressure and solubility, it is unstable with respect to *B*.

At the transition temperature, the solubilities and vapour pressures of *A* and *B* are the same.

The Vaporisation of Mixtures.

The following relations have been found between the partial pressures p_A and p_B of the liquids *A* and *B*, in mixtures containing x_A molecules of *A* (therefore $1 - x_A$ of *B*) in one total molecule, the pressures of the pure liquids at the temperature in question being P_A and P_B.

Let r_V be the ratio $\frac{\text{mols. } A}{\text{mols. } B}$ in the vapour, and r_L the ratio in the liquid.

Then by Dalton's Law of partial pressures:

$$\frac{p_A}{p_B} = \left(\frac{x_A}{1 - x_A}\right)_V = r_V \text{ and } \left(\frac{x_A}{1 - x_A}\right)_L = r_L .$$

The general relation was stated by F. D. Brown:

$$(r)_V = (r)^a{}_L \, k \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When $a = 0$ the liquids are immiscible.

If the partial pressures of *A* and *B* in vapour are proportional to the concentrations of *A* and *B* in liquid

$$p_A = P_A \, x_A, \, p_B = P_B \, (1 - x_A) \quad . \quad . \quad . \quad (2)$$

$$\text{or, } (r)_V = (r)_L \frac{P_A}{P_B} :$$

Suppose there is very little B, A being regarded as solvent:

Then, by Raoult's Law (Dilute Solutions)

$$\frac{\Delta p}{p_1} = \frac{n}{N}\ ;$$

or,

$$\frac{P_A - p_A}{p_A} = \frac{n_B}{n_A} = \frac{1 - x_A}{x_A} \qquad . \quad (3)$$

$$\therefore \qquad p_A = P_A\, x_A\,;$$

that is, the p_A, x_A and p_B, $1 - x_A$ graphs must in all cases be straight lines, when x_A and $1 - x_A$ respectively are large compared to 1.

The maximum work of mixing of two liquids, if x_A, p_A, P_A, etc., have the meanings stated above is given by the expression:

$$A_1 = RT\left(x_A \log \frac{P_A}{p_A} + (1 - x_A) \log \frac{P_B}{p_B}\right) \qquad . \quad . \quad (4)$$

for each molecule of mixture formed.

Or, if one molecule of A is mixed with x of B:

$$A_x = RT\left(\log \frac{P_A}{p_A} + x \log \frac{P_B}{p_B}\right) \qquad . \quad (4)$$

It can also be shown that:

$$x\,\frac{d \log p_A}{dx_A} + (1 - x)\,\frac{d \log p_B}{dx_A} = 0 \qquad . \quad (5)$$

or,

$$\frac{d \log p_A}{d \log x_A} - \frac{d \log p_B}{d \log (1 - x_A)} = 0 \qquad . \quad (5)$$

General Solution of Margules:

$$\left.\begin{aligned} p_A &= P_A x_A e^{\frac{\alpha_2 (1 - x_A)^2}{2} + \frac{\alpha^3 (1 - x_A)_3}{3}} \\ p_B &= P_B\,(1 - x_A)\,e^{\frac{(\alpha_2 + \alpha_3)\, x_A{}^2}{2} - \frac{\alpha_3 x_A{}^3}{3}} \end{aligned}\right\} \qquad . \quad (6)$$

The heat of vaporisation Q_{LV} of one component B associated with a second component A, can be calculated from the change of the partial pressure of B with the temperature, as in the case of the pure substance.

If the second component is non-volatile at the temperature in question, the partial pressure of B is, of course, identical with the total pressure.

Thus, if p'_2 and p$'_1$ are the vapour pressures of the solution, etc., at T_2 and T_1, p_2 and p_1, those of pure A, and Q^1_{LV} and Q_{LV} the quantities of heat evolved on condensation, then:

$$\log p'_2 - \log p'_1 = \frac{Q'_V}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \quad . \quad (1)$$

and so for p_2 and p_1:

$$\therefore \log\frac{p_2'}{p_2} - \log\frac{p'_1}{p_1} = \frac{Q'_{LV} - Q_{LV}}{R} \quad \frac{\Delta T}{T^2} \quad . \quad . \quad (2)$$

But $Q'_{LV} - Q_{LV} = Q_c$, the heat evolved by the condensed reaction, or mixture of liquid B with the stronger solution, lower hydrate, anhydrous salt, etc.

Salts usually dissolve in their saturated solutions with heat absorption; which is therefore the steeper P, T curve, that of water, or that of saturated solution?

Answer: The heat absorbed in the vaporisation of water from the saturated solution must be less than that absorbed by the vaporisation from water, since, in the former case, positive heat is evolved when the salt falls out, and is added to the negative heat of vaporisation. Q_{LV} absorbed is therefore less, and the p, T curve less steep in the first case.

PROBLEMS.

Additive Relations.

1. The rotation of the plane of polarisation of light by solutions of cane sugar is approximately proportional to the amount of sugar in the solution. It is also proportional to the length of solution traversed by the ray.

The wave-length of the light, and also the temperature must be defined.

The specific rotatory power is defined as the rotation brought about by 1 gram in 1 cubic centimetre of solution, the length of the column traversed by the ray being one decimetre.

If a is the rotation of the D line (sodium light) caused by a length, l decimetres, containing w grams in 1 cubic centimetre :

$$[a]_D = \frac{a}{l \times w} \text{ (specific rotation).}$$

The rotation caused by 2 decimetres of a solution of cane sugar at 20°, containing 20 grams in 100 grams in 100 cubic centimetres is $+ 26{\cdot}6$. Find $[a]_D$.

Answer **66·5.**

2. Deduce a formula for the relation between the rotation of a solution contained in a tube 2 decimetres long and the number of grams of cane sugar in 100 cubic centimetres of the contained solution. By means of this formula, determine the rotation of a solution containing 10 grams in 100 c.c., in a tube of this length.

$$[a]_D = 66^\circ{\cdot}5 = \frac{a}{l \times \frac{P}{100}}$$

P = grams in 100 c.c.

Hence, $P = 0{\cdot}752\ a$

$10 = 0{\cdot}752\ a$

$a =$ **13°·29.** Answer.

3. The value of $[a]_D$ for completely inverted cane sugar is approximately $-19{\cdot}66$ at 20°. A sample of pure cane sugar before inversion is found to have a rotation of $+ 13^\circ{\cdot}3$ in the 2 decimetre tube. After a partial inversion the rotation had fallen to $+ 2{\cdot}96$.

What is the weight of laevulose in the solution at this time?

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(dextrose)}}{C_6H_{12}O_6} + \underset{\text{(laevulose)}}{C_6H_{12}O_6}$$

Answer **3·158** grams of laevulose.

Find the grams of cane sugar originally present in 100 c.c. of solution; then the rotation for the corresponding amount of completely inverted sugar, from the value of $[\alpha]_D$.

The amount of inverted sugar can now be found by the method of proportional parts (equation 1, p. 89).

The grams of cane sugar inverted can then be transformed into grams of laevulose by the stoichiometrical equation.

4. The densities of equivalent normal salt solutions at a fixed temperature can be expressed in terms of a standard density (normal NH_4Cl, $D = 1{\cdot}0153$, at 18°), by the addition of specific increments Δ_A and Δ_B, due to the replacement of NH_4 by another kation B, and of Cl by another anion A.

$$D \text{ (normal } AB) = 1{\cdot}0153 + \Delta_A + \Delta_B.$$

If all the solutions are "m" normal:

D ("m" normal AB) $= D$ ("m" normal NH_4Cl) $+ m\Delta_A + m\Delta_B$.

The density of $N.\ NaCl = 1{\cdot}0388$ at 18°, that of $N.\ (NH_4)_2SO_4 = 1{\cdot}0313$. From these, combined with the density of $N.\ NH_4Cl$, find Δ for Na and for $\frac{1}{2}\,SO_4$, and the density of normal Na_2SO_4.

Answer $\Delta_{Na} =$ **0·0235.**

$\Delta_{\frac{1}{2}SO_4} =$ **0·0166.**

$D\ (Na_2SO_4) =$ **1·0548.**

5. The density of $2N.\ NH_4Cl = 1{\cdot}0299$, and $\Delta_{\frac{1}{2}Ba} = 0{\cdot}0739$. Find the density of $2\ N.\ NaCl$ and that of a solution containing 1 gram molecule of $BaCl_2$ per litre.

Answer $D\ (2\ N.\ NaCl) =$ **1·0769.**

$D\ (2\ N.\ BaCl_2) =$ **1·1777.**

(See Ewell, "Physical Chemistry".)

Dilute Solutions.

6. A solution containing 2·47 grams of ethyl benzoate, dissolved in 100 grams of benzene has a vapour pressure of 742·6 millimetres, at 80°; pure benzene having a vapour pressure of 751·86 millimetres, and a density of 0·8149 at the same temperature. Find the osmotic pressure of the solution.

$$\text{Deduce } P = \frac{\Delta p}{p_1} \times \frac{RT \times 1{,}000\, D}{M}$$

Equation (5), p. 90.

Answer $P =$ **3·78** atmospheres.

(Solute non-volatile; specific volume of the benzene unaltered in solution.)

Show that the osmotic pressure P of a solution freezing at ΔT° lower than the freezing point of the pure solvent, is equal to:

$$\frac{\Delta T \times Q_1 \times 1{,}000}{T_1 \times D}$$

T_1 being the freezing point of the solution, and Q_1 the molecular latent heat of fusion of the solvent in litre atmospheres per gram.

For, if V is the volume in litres of 1 mol. of solvent

$$PV = \frac{n}{N} RT_1 = \left(\frac{Q_M \Delta T}{RT\ T_1}\right) RT_1$$

and V litres $= \dfrac{MD}{1{,}000}$

$$\therefore\ P = \frac{Q_M \Delta T \times 1{,}000}{T \times M \times D}$$

7. A solution of ethyl benzoate in benzene freezes at a temperature lower by 0°·840 than the freezing point of pure benzene (see Table, p. 93).

If $Q_{SL} =$ 30·08 calories per gram, and D_L at the melting point = 0·8875, find the osmotic pressure of the solution.

Answer **4·25** atmospheres.

From the above data deduce $\Delta T_m = 5{\cdot}1$ for benzene, and from this, calculate directly the osmotic pressure. $P = CRT$.

Note.—Q and R must of course be expressed in the proper units.

8. The value of Q_{LV} for benzene at its boiling point 80°·2 is 93 calories per gram. What is the elevation of the boiling point ΔT_m for 1 mol., in 100 grams, and for 1 mol., in 100 cubic centimetres?

Answer **26°·5.**
32°·5.

9. 0·4559 grams of iodine dissolved in 30·14 grams of ether, raised the boiling point from 35° to 35°·126. The molecular weight of ether being 74·0, and $Q_{LV} = 90$ calories per gram, find the molecular weight of iodine.

Answer **252.**

Beckmann (*Zeitsch. physikal Chem.* (1890), 5, 76).

10. The latent heat of fusion of benzene is 30 calories per gram; $t_f = 5°·4$; find ΔT_m (1,000 grams).

Answer **5°·1.**

11. From the following experimental data, calculate ΔT_m (100 grams) for the solvent diphenyl $(C_6H_5)_2$, and the lowering of the freezing point produced by the addition of 0·3345 gram of CCl_4 to 10·779 grams of $(C_6H_5)_2$. The pure solid melts at 70°.

511 grams of water were added to 13·79 grams of $(C_6H_5)_2$ (liquid) at 70°·5.

The specific heat of water may be taken as 1·0, that of solid diphenyl = 0·386 (mean over the range 15°—70° C.).

The temperature rose from 15°·078 to 16°·41.

Answer $Q_{SL} =$ **28·5** calories per gram.
$\Delta T_m =$ **82·7.**
$\Delta T_{CCl_4} =$ **3°·13.**

The heat given out by the liquid $(C_6H_5)_2$ during solidification and cooling from 70°·5 to 16°·41 is sufficient to raise the temperature of the water by 1°·332. Hence, calculate Q_{SL} for one gram.

12. A solution containing 0·001 gram molecules of $ZnCl_2$ in 1,000 grams of water freezes at − 0°·0055, while one containing 0·0819 mol. freezes at − 0°·3854.

ΔT_m for water being taken as 1·89, find the number of osmotically active molecules (i) in one stoichiometrical molecule of $ZnCl_2$.

Answer **2·91.**
2·49.

H. C. Jones (*Zeitsch. physikal Chem.* (1893), 11, 547).

13. Five grams of silver nitrate, dissolved in 1,000 grams each of ethyl, alcohol and water, raise the boiling point by 0°·0348 and 0°·0306, respectively. Find the molecular complexity of the silver nitrate in the two solvents.

Answer **0·98** $AgNO_3$ (in ethyl alcohol).
0·5 $AgNO_3$ (in water).

14. The following are values of the elevation of the boiling point, when naphthalene ($C_{10}H_8$) is dissolved in chloroform.

The boiling point of chloroform is 61°·2.

Q_{LV} (1 gram) = 61·0.

60·81 grams of chloroform were used throughout.

Grams $C_{10}H_8$	ΔT
1·0171	0·475
2·0266	0·942
5·0695	2·320
7·0898	3·205

$M\ (C_{10}H_8) = 128.$

Beckmann (*Zeitsch. physikal Chem.* (1890) 6).

Calculate ΔT_m (100 grams solvent) from Q_{LV}, and from the experimental data, by plotting the grams of $C_{10}H_8$ against ΔT_m and extrapolating to infinite dilution.

Answer ΔT_m = **36·6** from Q.
ΔT_m = **36·4, 36·2, 35·6, 35·2.**

15. Find a formula for the molecular elevation of the boiling point of water (ΔT_m 100 grams) from the formula

$Q = 606{\cdot}5 - 0{\cdot}708t°$; also the values of the constant ΔT_m at $t° = 70°$ and $t° = 100°$.

Answer **4·2.**
5·2.

$$\Delta T_m = \frac{0{\cdot}02\,(273 + t)^2}{606{\cdot}5 - 0{\cdot}708t}.$$

16. Five grams of benzoic acid dissolved in 100 cubic centimetres of water lowers the freezing point by 0° 24; dissolved in 100 cubic centimetres of benzene ($D = 0{\cdot}9$) this quantity lowers the freezing point by 0°·67. What is the molecular weight in the two solvents?

Answer **388.**
422.

17. For non-associated solvents the ratio $\frac{Q_{LV}}{T_b} = 20{\cdot}6$, on the average. Hence, prove that ΔT_m (1,000 grams solvent) $= 0{\cdot}000096\ MT_b$.

$$\Delta T_m = \frac{RT^2M}{Q_1\ 1{,}000}$$

Also, find approximately ΔT_m for ethyl acetate. (See table.)

Answer **2·94.**

18. What is the molecular lowering of the freezing point for 1 mol. of a solute, dissolved in 100 mols. of (*a*) benzene, (*b*) nitrobenzene?

Answer **0·0653°** (*a*).
0·059° (*b*).

19. If ΔT_m is the molecular lowering of the freezing point for 1 mol. of a solute in 1,000 grams of a solvent, and $\frac{Q_{SV}}{T_f}$ is a constant, show that the lowering for 1 mol. in 1,000 mols. of solvent divided by the freezing point is also a constant, and equal to 0·00023° for benzene, and to 0·00021° for nitrobenzene.

$$\frac{\Delta Tm}{MT} = \frac{RT}{1{,}000\ Q_M}.$$

20. To what accuracy in degrees must the thermometer be read in order to secure a 1 per cent. accuracy in the molecular weight of a substance, of which $m = 200$ under the following conditions:

One gram is dissolved in 100 grams each of (1) water, (2) benzene, and the methods of (*a*) freezing point, (*b*) boiling point, are used?

Other errors being excluded, the percentage error of m is the same as that of ΔT_m.

Answer (1) (*a*) **0·001°** (*b*) **0·0002°**.
(2) (*a*) **0·003°** (*b*) **0·001°**.

21. An amalgam containing 1·142 grams of tin dissolved in 100 grams of mercury was heated in the vapour of mercury, boiling at a pressure of 768·8 millimetres. The vapour pressure over the amalgam was 754·1 millimetres. What is the molecular weight of the dissolved tin?

Answer **117·4.**

$$m = \frac{p_1}{\Delta p} \cdot \frac{wM}{W}$$

Ramsay (*Journ. Chem. Soc.* (1889), 55, 532).

22. The saturation pressure of aqueous vapour at 17·0° being 14·395 millimetres, find that over a 1 per cent. solution of (1) urea ($CO(NH_2)_2$), (2) cane sugar ($C_{12}H_{22}O_{11}$), and (3) potassium chloride (KCl), assuming the two former to be present as single molecules, and the latter to be fully dissociated.

Also, what will be the osmotic pressures of the three solutions?

Answer (1) $p =$ **14·35** mm.
$P =$ **4·03** atm.

23. It has been observed that the melting point of silver in air is 955°; in a vacuum, 962°. Nitrogen does not dissolve in silver.

When 10 grams of molten Ag are kept in contact with oxygen at a pressure of 760 millimetres, they absorb 21·35 c.c. of O_2, measured at N.T.P. (See Problem 70, p. 214.)

If Q_{SL} for 1 gram of Ag at its melting point is 24·7 cal. (Pionchon), and 1 c.c. of O_2 at N.T.P. weighs 0·001429 gram, calculate the melting point of Ag in air from its melting point in a vacuum.

Answer $\Delta T = \mathbf{10{\cdot}4^\circ}$.

$T_1 = \mathbf{951{\cdot}5^\circ}$.

Donnan & Shaw (*Journ. Soc. Chem. Ind.* (1910), 29, 988).

24. What will be the ratio of the vapour pressures of two solutions, containing respectively $n_2 = 1$ and $n_1 = 0{\cdot}36$ mol. of H_2SO_4 in 1,000 grams of water, if the mean value of i for H_2SO_4 in this range of concentrations is 2·22 ?

Answer $\frac{p_1}{p_2} = 1{\cdot}026$.

$$\log \frac{p_1}{p_2} = \frac{n_2 - n_1}{N \times 2{\cdot}3}.$$

Dolezalek ("Lead Accumulator").

25. The actual vapour density of acetic acid (CH_3COOH) is 1·61 times the theoretical density at its boiling point, under normal pressure. Compare the actual vapour pressure in a solution containing 1 mol. of a non-volatile solute in 1,000 grams of acetic acid, with that which would be observed if the acetic acid were not associated.

Answer $p_1 = \mathbf{692}$ mm. (observed).

$p_1 = \mathbf{716}$ mm. (theor.).

If p_1 is the vapour pressure when 1 mol. is dissolved in 1,000 grams,

$$\frac{p - p_1}{p_1} = \frac{M}{1{,}000}.$$

Raoult and Recoura, Van't Hoff.

26. Iodine is known to be dissolved in benzene as I_2. When the solution is frozen the solid which separates is found to contain I_2. This I_2 is known to be in solid solution, because the ratio between the percentage of I_2 in the solid and in the liquid is constantly 0·357.

Hence, find what should be the value of ΔT_m for C_6H_6 and I_2.

Note that if $C_L = KC_S$ (concentration of iodine in the liquid and solid phases), the molecular weight of the iodine must be the same in each phase. (See p. 107.)

It is also necessary to show that if $\Delta T'_m$ is the lowering of the freezing point which would be observed, if the solvent separated as a pure solid:

$$\Delta T_m \text{ (obs.)} = \Delta T'_m \left\{ 1 - \frac{\left(\frac{n}{N}\right)_S}{\left(\frac{n}{N}\right)_L} \right\}$$

Answer **3·48.**

(See Introduction, p. 92.)

$$\Delta T'_m = \frac{RTT_1}{Q \times 1{,}000} \left\{ (n)_L - (n)_S \right\}$$

n and n_S being the number of mols. in 1,000 grams of the liquid and solid.

Bruni (" Uber Feste Lösungen," Ahrens Sammlung VI.)

27. A correction may be made for the volatility of the solute by means of equation (11), p. 92.

Two liquids A and B, mixed in the molecular proportion stated below, boiled at 300° C., and the solute was found by analysis to constitute $\frac{1}{100}$ of the volume of the vapour. If the boiling point of pure A is 299° and Q_M for $A = 1{,}200$, find the ratio $\left(\frac{n}{N}\right)_L$

Answer **0·0167.**

If the solute were not volatile, what molecular concentration would be required for the same elevation of the boiling point?

Answer **0·0067.**

28. Two grams of a substance of unknown molecular weight raises the boiling point of 100 grams of ethyl ether ($\Delta T_m = 21{\cdot}2$) by 0·2°), and the same quantity in 100 grams of aniline ($\Delta T_m = 32{\cdot}2$) raises the boiling point by 0·1°. Find the composition by weight of a small quantity of liquid distilled from a large quantity of boiling aniline solution.

The substance is supposed to be non-volatile at the boiling point of ether.

Answer **1·272** grams in **100** grams of aniline.

First find m from the ether data, then calculate normal $\Delta T'$ for this quantity of solute dissolved in aniline, and if ΔT is the actual elevation observed:

$$\Delta T' = \Delta T_m \, n_L \quad \Delta T = \Delta T_m \, (n_L - n_V).$$

Phase Rule.

The concentration, temperature and pressure, temperature relations of the system phenol and water have been fairly completely investigated. The literature bearing on the subject includes:

Alexejew	(*Wied. Ann.* (1886), 28, 306).	
Rothmund	(*Zeitsch. physikal Chem.*	(1898), 26, 433).
Jones	(,, ,, ,,	(1889), 4, 502).
Eykman	(,, ,, ,,	(1889), 4, 502).
Schreinemakers	(,, ,, ,,	(1900), 35, 462).
Meerburg	(,, ,, ,,	(1902), 40, 673).
Bancroft	(" Phase Rule ").	

From the results the following have been selected, and used in the construction of the diagram.

The answers to the problems may be obtained by measurement from the diagram, or, better, from a plotted graph on a larger scale.

The concentrations are given as grams of phenol in 100 grams of the mixture.

Two liquid layers (1) aqueous, poor in phenol; (2) phenolic, rich in phenol.

	(1)	(2)		(1)	(2)
t	C_1	C_2	t	C_1	C_2
20	8·40	72·24	50	12·08	62·83
25	8·71	71·38	55	13·88	60·18
30	8·92	69·95	60	17·10	56·10
35	9·34	68·28	65	22·26	49·34
40	9·78	66·81	68·8	35·90	35·90
45	10·62	65·02			

Solid Phenol and Solution.

t	C
+ 5°·5	83·36
19·5	92·97
32·0	97·18

Ice and Solution (C grams phenol in 100 c.c. solution).

t	C
− 0·01	1·2
− 0·619	58·21

Invariant point (ice, solutions, vapour).
About − 0·9

Invariant point (phenol, two solutions, vapour).
About + 1·5.

Percentage of phenol in liquid (C_1) and in vapour (C_2) at 56·3° (P = about 125 mm.).

C_1	C_2
2·0	2·55
5·58	5·47
7·42	6·57
10·88	7·42
14·5 and 59·0	7·83

29. A mixture of 30 grams of phenol and 70 of water ("*a*" on diagram) is kept at 30°. What are the amounts and compositions of the phases?

Answer **65·39** grams of aqueous solution.
34·61 grams of phenolic solution.

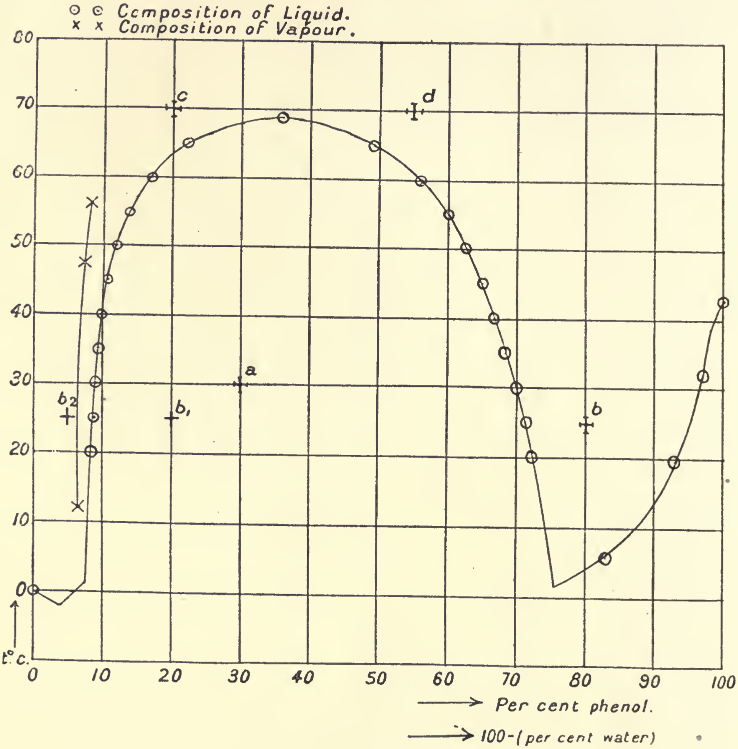


Fig. 7.

Let x and $100 - x$ be the amounts of each phase.

$$\text{Total phenol} = \frac{8{\cdot}9 \times x}{100} + \frac{10{\cdot}0\,(100 - x)}{100} = 30$$

$$x = 65{\cdot}39$$

30. (1) What are the nature, number and composition of the phases corresponding to the points b, b_1 and b_2 on the diagram, so far as they can be known from the above data?

(2) Also, how will the pressure and composition of the vapour and the composition of the liquids be affected if successive quantities of phenol are added to each of the above mixtures?

Answer:—

(1) **b** is a **homogeneous solution** containing **80** per cent. of **phenol** (vapour concentration unknown).

b_1 is a system composed of **two layers of liquid** containing **8·7** and **71·4** per cent. of **phenol** respectively. The **vapour** contains **7·7** per cent. of **phenol.** The amounts of the two liquids, of course, depend on the amounts of vapour, but it would usually be understood that this was small compared to the amounts of liquid or solid.

b_2 denotes a **homogeneous solution** containing **5** per cent. of **phenol.** The (small) amount of vapour contains less than 7·7 per cent. of phenol.

Answer:—

(2) **b** The added phenol **dissolves** and finally remains undissolved.

b_1 The phenol **dissolves,** with the formation of more phenolic solution until the aqueous layer is gone. During this time the pressure and concentration of the vapour remains constant.

b_2 **Phenol dissolves** until the solution contains 8·7 per cent., then **two layers** are formed. The vapour also becomes richer in phenol up to 7·7 per cent.

31. How much phenol and water must be added to "*b*" to cause a separation of a new phase in each case?

Answer **507** grams of phenol.
12·05 grams of water.

$$\frac{80 + x}{100 + x} = 0{\cdot}967 \qquad 0{\cdot}033\,x = 16{\cdot}7$$

$$\frac{20 + x}{100 + x} = 0{\cdot}286$$

32. Solutions *c* and *d* on the diagram are cooled from 70°. At what temperature does another liquid layer appear in each case?

Answer (*c*) **63·5°.** (*d*) **61·0°.**

33. A mixture of 30 grams of phenol and 70 grams of water was distilled at 56°·5. What are the amounts and compositions of the two solutions at the beginning of the distillation, and what weight of the mixture must be distilled before the aqueous layer vanishes?

Answer **65·16** grams of aqueous liquid at the beginning.
56·67 grams are distilled before the system becomes bivariant.

34. In this, as in other cases characterised by the formation of two liquid layers, the sum of the concentrations of the phenol in the aqueous and phenolic parts is a linear function of the temperature. This regularity will recall the law of the rectilinear diameter which connects the densities of a liquid with those of its saturated vapour (p. 80).

Draw the rectilinear diameter in the case of phenol and water, and determine the constants in the formula:

$$C_1 + C_2 = A + Bt.$$

Answer $A =$ **83·62.** $B = -$ **0·167.**

35. The same relation holds in the case of propionitril and water. Determine the critical solution temperature from the following measurements:

t	C_1	C_2
40	10·7	92·1
60	12·7	88·5
100	22·4	75·5

Answer: The liquids are **completely miscible** at temperatures **above 113°**.

Rothmund (*loc. cit.*, on p. 108).

The following table gives the composition of the liquid in equilibrium with the solid phases of a mixture of para-toluidine and phenol at different temperatures.

J. C. Philip (*Journ. Chem. Soc.* (1903), 83, 829).

Conversely, of course the temperatures are the initial freezing points of the liquids of stated composition.

The compositions are expressed in molecules per cent. of toluidine and may be plotted as the abscissæ of a concentration temperature diagram, the ordinates being the initial freezing points.

The composition of the solid on each continuous branch of the curve is constant.

Prove by the phase rule that this must be the case.

At each discontinuity (invariant point) a new solid phase appears.

36.

Mol. per cent. of para-toluidine.	*Freezing point.*
0·0	40·4
5·6	35·5
11·5	29·0
15·4	23·5
18·9	18·1
21·4	13·4

Mol. per cent. of para-toluidine.	*Freezing point.*
25·3	9·5
29·2	15·3
32·5	20·4 and 19·4
38·0	25·6 ,, 24·3
42·1	28·0 ,, 26·5
46·8	29·5 ,, 28·0
49·8	30·0 ,, 28·5
55·3	28·8 ,, 27·5
59·8	27·0 ,, 26·0
64·1	24·3 ,, 23·7
68·0	20·6 ,, 19·7
70·1	20·3 ,, 19·9
73·3	23·9
80·3	30·5
87·5	35·9
100·0	42·8

Plot these results on graph paper and determine the eutectic temperatures and compositions, and the composition and melting point of any compound formed.

Answer : The eutectic temperatures (invariant systems) are **8°** and **20°**.

The eutectic compositions are **24** and **69** molecular per cent. **toluidine.**

The compound contains equimolecular proportions of the two components and melts at **28·5°** and **30°**, therefore it occurs in two modifications.

37. What are the physical states of mixtures containing 10, 25, 50, 70 and 90 per cent. of para-toluidine, and kept at 25°?

Answer : **Solid, liquid, solid, liquid** and **solid.**

38. Denoting by *a*, *b*, *c*, *d* and *e* the points on the graph described in the last problem, find at what temperatures new phases will appear when the liquids are cooled and the solids heated.

Answer *a* melts at 30·5°.
c ,, ,, 28·5° or 30°.
e ,, ,, 37·3°.
b freezes at 9·8°.
d ,, ,, 20·7°.

39. What is the greatest possible yield of pure para-toluidine from 100 total mols. of *e*?

Answer 67·7 mols.

40. How much para-toluidine must be added to 100 mols. of the mixture *a* to bring about complete liquefaction at 25° and at 15°?

Answer 5·9 mols.
13·9 ,,

The following numerical data and diagram will serve to illustrate the complete p, T and C, T relations of water and a salt forming two hydrates.

(See the account of the hydrates of $CaCl_2$—Roozeboom, *Zeitsch. physikal Chem.* (1889), 4, 31).

In the diagram the pressures on the left (in millimetres of mercury) refer to the systems up to the point *o*, and the temperatures up to 50°. The same point *o* is the starting point of the diagram on the right, from $t = 50°$ to $t = 200$, p being expressed in centimetres of mercury.

Corresponding points on the pressure and concentration diagrams are marked by the same small letters.

The invariant, univariant and bivariant systems (two components in four, three and two phases respectively) represented by points, lines and areas on the p, T diagram are named according to the phases present. The abbreviations used are:

Anhydrous salt = *A*.
Solution = *Sol.*
Vapour = *V*.

The tetrahydrate ($A + 4\ H_2O$) = 4.
The monohydrate ($A + 1\ H_2O$) = 1.

The C, T diagram is similar to those already described.

The concentrations of salt C are expressed as mols. of salt in 100 mols. of solution; therefore the corresponding concentrations of water are $100 - C$.

$t°$	C	$t°$	C	$t°$	C
— 10°	5	34	18·0 and 25·0	80	45·5
— 5°	3 and 5·5	34·5	24·0 ,, 25·5	90	49·0
0	0 ,, 6	35	20·0	100	53·0
5	6·5	40	30·5	120	61·0
10	7·5	43	34·0	140	70·0
20	10·0	45	38·0	160	79·5
25	12·0	50	38·5	180	89·5
30	14·5	60	40·0	190	95·0
32	16·0	70	42·5	200	100·0

Anhydrous salt melts.

System 4 + *Sat. Soln.* + *V.*

$t°$	p	$t°$	p
— 10	1·9 (ice)	27·5	10·0
0	3·25	30·0	10·0
5	4·5	32·5	9·5
10	6·0	35·0	7·0
20	8·8	34·0	5·0
25	9·75		

System 4 + 1 + *V.*

$t°$	p
25	1·3
27·5	1·8
30·0	2·5
32·5	2·75
34·0	5·0

System 1 + *Soln.* + *V.*

$t°$	p
34	5·0
35	5·25
40	7·0
45	10·0

A + 1 + *V.*

$t°$	p
25	1·0
30	1·25
35	2·4
40	4·0
43·5	6·25
45·0	10·0

System A + Soln. + V.

t°	p (cm.)	t°	p (cm.)	t°	p (cm.)
50	2	100	25·0	160	98·0
60	3	120	55·0	170	87·0
70	5	135	88	180	66
80	9	140	94	190	28
90	15·5	150	99·5	200	0

Ice and Vapour.

t°	p
— 10°	1·9
— 5	3·0
0	4·6

Water and Vapour.

t°	p
0°	4·6
10°	9·2
20	17·5

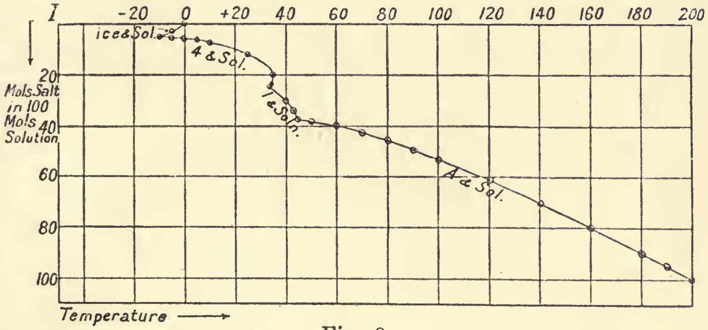


Fig. 8.

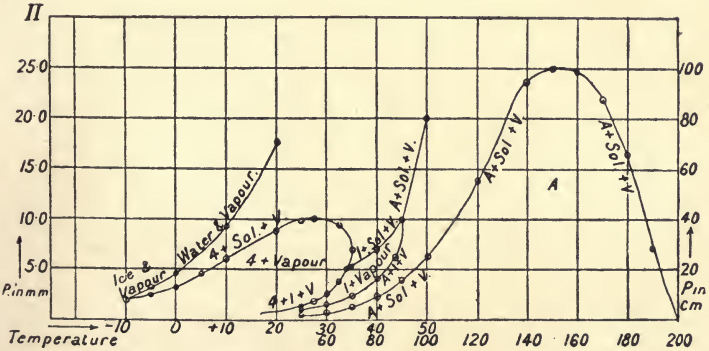


Fig. 9.

The most complicated relations are met with during the dehydration of the unsaturated solution at $t^\circ = 34{\cdot}5^\circ$.

At $C = 18{\cdot}5$ and $p = 8{\cdot}2$ millimetres, 4 begins to deposit. As this makes the solution weaker, dehydration and deposition can proceed together at constant pressure and temperature, until it is all solid 4. Dehydration then proceeds at changing pressure, until some solution of $C = 24{\cdot}0$ (therefore containing more A than the tetrahydrate) is formed. The whole then liquefies with dehydration at $p = 5{\cdot}5$, then p and C change to 5·25 and 25·5, at which they remain constant while 1 is deposited.

When all is solid the pressure falls to 2·3, and remains constant until solid 1 has passed into solid A, then falls to zero.

41. Describe similarly the process of dehydration at 25° and at 34°.

Answer (25°). Steady values of p are:
9·75, 1·3 and **1·0.**
Successive systems are:
4 + soln. ($C = 12$), **4 + 1** and **1 + A.**

Answer (34°). Steady values of p are:
8·5, 5·0 and **2·2.**
Successive systems are:
4 + soln. ($C = 18$), **4** alone while p is changing, **4 + 1** while 4 is changing into 1, and **1 + A** while 1 is changing into A.

42. A mixture of 5 mols. of water with 95 mols. of A was placed in tubes which were subsequently evacuated, sealed, and heated to 122·5°, 145° and 180°. What are the equilibrium pressures of water-vapour at the three temperatures?

Answer $p =$ **60·5, 98,** and **65** cm. *Hg.*

43. At what temperature will a saturated solution have a maximum of vapour pressure, and what is this maximum and the corresponding concentration of the solution?

Answer **152° — 154°.**

$p = $ **100** cm. of mercury. $C =$ **76·5.**

44. What fixed points of temperature (invariant) could be obtained with this system?

Answer **— 10°, + 34°, 35°, 45°** and **130°.**

Describe these points, and say how each would be obtained in practice.

45. A mixture of 10 mols. of water with 200 mols. of anhydrous salt (A) is heated in an evacuated sealed tube to (1) 170°, (2) 185°.

Predict the composition and quantity of the phases present immediately after breaking open the tubes kept at those temperatures.

Answer (1) **200** mols. of anhydrous salt.

(2) **85** mols. of **A** and a **solution** containing **115 mols.** of **A** and **10 mols.** of water.

46. Solutions containing anhydrous salt (A) and water in the molecular proportions: (1) 5 to 95; (2) 15 to 85; (3) 20 to 80; (4) 34 to 66; (5) 45 to 55 respectively are cooled from 100°.

State (*a*) the temperature halt points;

(*b*) the amount and composition of the phases when all has become solid.

Answer 1. (*a*) **— 10°.**

(*b*) **25** total mols. of mixture as **4,** and **75 of ice,** or **5** mols. of **4** and **75** mols. of **ice.**

2. (*a*) **31° — 10°.**

(*b*) **13·333** mols. of pure **4** are separated between **31°,** at which point crystallisation begins, and — **10°.** Then ice and **4** are separated alternately, and the final composition of the solid conglomerate is **15** mols. of **4** and **25** of **ice.**

3. (*a*) **35°.**
   (*b*) **20** mols. of pure **4.**
4. (*a*) **43°, 34°.**
   (*b*) **53⅓** mols., as **4** and **46⅔** as **1.**
5. (*a*) **78°** (momentary), **45°, 34°.**
   (*b*) **16⅔** mols. as **4**, and **83⅓** as **1.**

For the calculation of amounts, see Problem 31, p. 112.

Thus, in the second case, if x mols. of A separate as $A + 4\ H_2O$, the amount of 4 which has separated before ice appears at $-10°$, is given by the ratio:

$$\frac{15 - x}{85 - 4x} = \frac{5}{95} \qquad \therefore \quad x = 13{\cdot}33.$$

That is to say, 66·7 total mols. of the mixture separate as 4 (13·3 of A and 53·4 of crystal water), leaving a solution of 15 — 13·333 of A, and 85 — 53·333 of water, from which ice and 4 separate alternately, as in case (1). The relative quantities must obviously be:

$$1{\cdot}667\ A + 4 \times 1{\cdot}667\ H_2O \text{ as } 4$$

and $$31{\cdot}667 - 6{\cdot}667 = 25\ H_2O \text{ as ice.}$$

47. Construct a pressure-temperature and concentration-temperature diagram for the system Na_2SO_4, water.

The concentrations are given in grams of anhydrous salt, to 100 grams of water, and the pressures in millimetres of mercury.

Solubility of $Na_2SO_4\ 10\ H_2O$.

$t =$	0	10	15	20	25	30	34
$C =$	5·0	9·0	13·2	19·4	28·0	40·0	55·0

Solubility of Na_2SO_4.

$t =$	35	40	50	60	70	80	90	100
$C =$	49·4	48·2	46·8	45·5	44·5	43·7	42·9	42·7

Solubility of $Na_2SO_4\ 7\ H_2O$.

$t =$	0	10	20	26
$C =$	19·6	30·5	44·7	55·0

Solubility of Na_2SO_4.

$t =$	18	20	25	30	35	40	50	60	70	80	90	100
$C =$	53·3	52·8	51·5	50·4	49·4	48·2	46·8	45·5	44·5	43·7	42·9	42·7

Vapour pressures of Saturated Solutions.

$t°$	p $Na_2SO_4 + Soln.$	p $Na_2SO_4\ 10\ H_2O + Soln.$
28·3°	24·07	26·20
30·1°	26·60	28·03
32·6	30·82	30·82

48. The three systems:—(1) $Na_2SO_4 + Na_2SO_4 . 10\ H_2O$; (2) $Na_2SO_4 . 10\ H_2O$ + saturated solution; (3) Na_2SO_4 + saturated solution, are put in separate, evacuated vessels with free communication by means of their vapour. What are the possible final states, the temperature being 29° throughout?

Answer **$Na_2SO_4 . 10\ H_2O$ + saturated solution.**
(with water in excess through the whole system).
$Na_2SO_4 + Na_2SO_4 . 10\ H_2O$.
(with Na_2SO_4 in excess),
or all **$Na_2SO_4 + 10\ H_2O$**
(with the required ratio of salt to water).

49. If the above-mentioned systems are used as drying agents, and the rate of drying is proportional to the affinity of each for water-vapour, what are the relative rates? (See pp. 97, 98.)

Answer 1 : 2 : 3 as 0·0955 : 0778 : 0444.

50. What are the compositions of the three saturated solutions in equilibrium with $Na_2SO_4 . 10\ H_2O$, Na_2SO_4

. 7 H_2O and Na_2SO_4, at 19°, and what will be the effect of adding a small crystal of $Na_2SO_4 . 10 \; H_2O$ to each ?

Answer In 100 grams of water there are dissolved : (1) 18 ; (2) 43 ; (3) 52·5 grams of anhydrous salt. So much decahydrate will be deposited in cases (2) and (3) as is necessary for the attainment of the equilibrium concentration of the system :

decahydrate + solution.

51. What are the temperatures corresponding to the transitions :

(1) $Na_2SO_4 \; 10 \; H_2O \longrightarrow Na_2SO_4$
(2) $Na_2SO_4 \; 7 \; H_2O \longrightarrow Na_2SO_4$
(3) $Na_2SO_4 \; 10 \; H_2O \longrightarrow Na_2SO_4 \; 7 \; H_2O$.

Answer (1) **32·4°.**
(2) **24·5°.**
(3) The **heptahydrate is unstable** with respect to the **decahydrate** over the whole range of solubilities investigated, but the curves would indicate a transition temperature of about **36°**, if the formation of anhydrous salt could be prevented.

52. Verify the following statements by means of the phase rule.

A saturated solution of A and B in presence of the two solid salts has only one degree of freedom.

How many degrees of freedom has a system of solid A, $A + B$ solution and vapour ; also how many degrees of freedom has the same system with the addition of (1) ice ; (2) B and ice to the solid phases ?

Answer **2, 1 and 0 degrees of freedom.**

53. The qualitative concentration, temperature relations may be seen at a glance from the diagram below, which represents the solubilities of *NaCl* and *KCl* in presence of one another.

Show that the effect of evaporating any given unsaturated solution, denoted by a point P, is to change the concentrations upwards along the line joining P and the origin O.

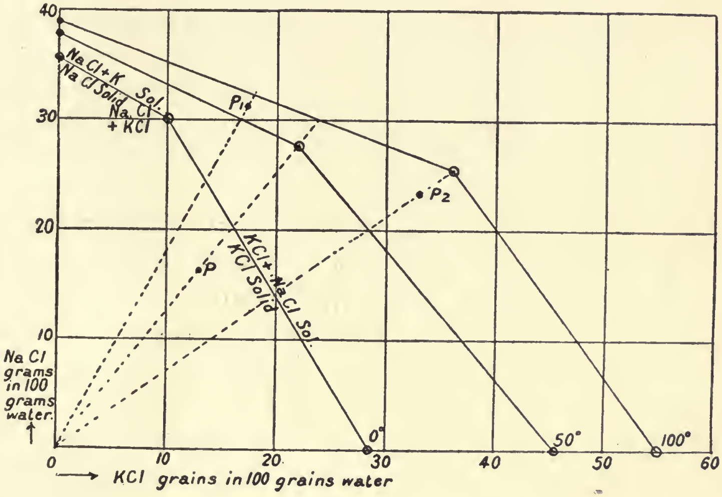


Fig. 10.

54. Which salts will be first deposited:

(1) On the evaporation of unsaturated solutions of composition P, at 0°, 50° and 100°?

(2) On crystallisation at 50° of the supersaturated solutions P, and P_2, and on the evaporation of P_2 at 100°?

Answer (1) **KCl, KCl + NaCl, NaCl.**

(2) **NaCl, KCl, NaCl + KCl.**

55. The following are the compositions of saturated solutions in equilibrium with the solid phases at the head of the columns.

Solid Phase.

t	$NaCl$	KCl	$NaCl + KCl$	
0°	35·6	28·5	30	10
50°	36·7	42·9	27·5	22
100°	39·1	56·6	25·5	36

The concentrations are expressed in grams of salt to 100 grams of water.

Assuming the isothermals to be straight between these experimental points, as in the diagram, find the nature and amounts of the salts deposited after each of the following successive operations, on 1,000 grams of water originally saturated with both salts at 100°.

(1) The solution cooled to 0°.

(2) The solution heated to 100° again, and evaporated until KCl begins to come down, then decanted hot.

(3) The decanted solution cooled to 0°.

Answer (1) **232·5** grams of KCl deposited.
(2) **184·1** ,, ,, $NaCl$,,
(3) **92·1** ,, ,, KCl ,,

56. A saturated solution of $NaCl$ and KCl at 100°, containing 500 grams of water is cooled to 50°. How much salt separates?

Answer **62·5** grams of KCl.

57. An unsaturated solution, containing 24·3 grams each of $NaCl$ and KCl, is evaporated (1) at 50°; (2) at 100°. What weight of each pure salt is precipitated before both begin to fall out?

Answer (1) **6·2** grams of KCl.
(2) **8·2** grams of $NaCl$.

The relations between the concentration, temperature and nature of the solid phases for a pair of salts which are capable of forming hydrates and a double salt are best exemplified in the case of the naturally occurring carnallite KCl, $MgCl_2$ 6 H_2O (Stassfurt deposit). The commercial utilisation of this salt chiefly depends upon the separation of the more valuable KCl from $MgCl_2$.

The diagram numbers are taken from an original paper by Van't Hoff and Meyerhoffer (*Zeitsch. physikal. Chem.* (1899), 30, 64).

The concentrations of $MgCl_2$ and KCl, expressed as mols. of salt to 1,000 mols. of water, and in equilibrium with the various solid phases, at the temperatures given by the abscissæ, appear as lines.

The invariant points are lettered as in the accompanying table, and corresponding points on the $MgCl_2$ and the KCl parts of the diagram are marked by the same letter.

In order to solve the problems, the whole may advantageously be plotted on squared paper. A suitable scale is 1 millimetre = 1°, and 1 millimetre = 1 mol. of salt.

It must not be forgotten that the problems refer to equilibrium conditions, and that in practice the phenomena of supersaturation, suspended transformation, etc., may sometimes completely alter the nature of the results.

COMPOSITION OF SOLUTION.

Letter	$t°$	*Solid Phases.*	*Mols.* $MgCl_2$	*Mols.* KCl
C	−11·1	*ice* + KCl	—	59·4
B	−33·6	*ice* + 12 ($MgCl_2\ 12\ H_2O$)	49·2	—
D	−34·3	*ice* + KCl + 12	43	3
E	−21·0	C (carnallite $KCl\ MgCl_2$ 6 H_2O) + 12 + KCl	66·1	4·9
E_1	0	C + KCl	67·1	7·3
E_2	25	,, ,,	72·7	11·5
E_3	61°·5	,, ,,	80·6	17·4
E_4	154°·5	,, ,,	124	34
M	167°·5	,, ,,	166·7	41·7
F	−16·6	12 + C	84·0	small

Composition of Solution—*continued.*

Letter	$t°$	*Solid Phases*	*Mols.* $MgCl_2$	*Mols.* KCl
G	$-16·9$	$12 + 8 + C$	87·5	small
H	$-3·4$	$8 + 6 + C$	99	small
H_1	25°	$6 + C$	105	2
J	115°·7	$6 + 4 + C$	162	4
K	152°·5	$4 + KCl + C$	200	24
L	176°	$4 + 2 + KCl$	240	41
N	186°	$2 + KCl$	240	63

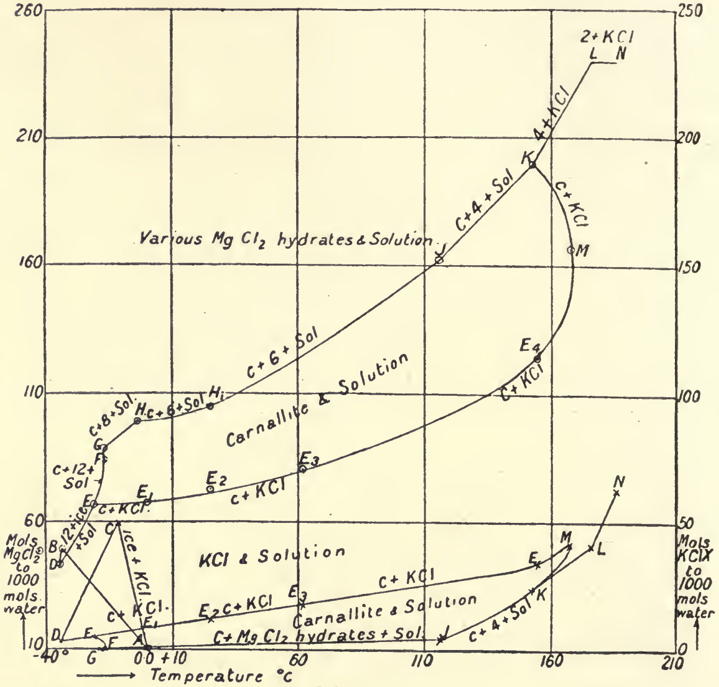


Fig. 11.

58. A saturated solution at 25°, containing 1,000 mols. of water, and 5 mols. each of solid 6 and carnallite, is treated with solid KCl, until the latter just ceases to dissolve.

What is the final composition of the solution, and the weight of the solid carnallite formed?

Answer The solution contains **47·8** mols. of $\mathbf{MgCl_2}$; **7·55** mols. of **KCl** and **656·8** mols. of $\mathbf{H_2O}$.

The total carnallite present at the end = **67·2** mols.

At the beginning, the solution contains 47·8 mols. of $MgCl_2$, 2 mols. of KCl, and 1,000 mols. of H_2O in presence of the solids.

The addition of KCl first converts 6 into C, without altering the composition of the solution. When 6 is all converted, the KCl concentration increases and that of the $MgCl_2$ decreases (by precipitation as C), until E_2 is reached, the solution now being saturated with respect to KCl.

From the composition of this solution, combined with the fact that each mol. of C requires for its formation 6 mols. of water, there is obtained the following equation:

If x = mols. of C precipitated,

$$\frac{\text{Dissolved } MgCl_2}{\text{Water in solution}} = \frac{105 - x}{1{,}000 - 6x} = \frac{72{\cdot}7}{1{,}000}.$$

Whence $x = 57{\cdot}2$.

The solution must contain 105 — 57·2 mols. of $MgCl_2$, and therefore 7·55 mols. of KCl, and 656·8 mols. of water.

59. Fifty mols. of carnallite was treated with the quantity of water, just sufficient to bring all the $MgCl_2$ into solution, at 60°.

State the quantity of water, and the weight of pure KCl obtained.

Answer **37·5** mols. of water.
38·8 mols. of KCl.

60. A similar operation to that described in the last problem was performed at 150°.

Find the quantity of water required to dissolve all the

$MgCl_2$ present in 50 mols. of carnallite, and compare the percentage yield of pure KCl with that obtained at 60°.

Answer **130** mols. of water.
72·4 per cent., as against **77·5** per cent. at **60°**.

61. One hundred mols. of carnallite is melted in its own water of crystallisation.

Supposing it be possible to centrifuge the crystals completely free from the mother liquor, how much pure KCl will be obtained?

Answer **75** mols.

62. What are the highest and lowest possible concentrations of $MgCl_2$ and of KCl with which carnallite can exist at 25°?

(See Table, pp. 125, 126.)

63. One mol. of carnallite is mixed with 1 mol. of $MgCl_2 \cdot 4\,H_2O$ at 152°·5.

What is the final condition of the system, if no water is allowed to evaporate?

Answer The mixture liquefies, depositing **0·76** mols. of KCl.

The Vaporisation of Mixtures.

64. If the relation connecting the partial vapour pressures of the liquids A and B with the composition of the mixed liquid $x_A\,(A) + 1 - x_A\,(B)$ is known, the behaviour of the liquids on distillation, the composition of the distillate from any mixture, as well as the affinity of mixing and demixing may easily be calculated.

(See Introduction, p. 97.)

Thus, let the two liquids obey the law:—

$$p_A = P_A\,x_A \qquad p_B = P_B\,x_B.$$

Now, if $P_A = 0{\cdot}5$ atmosphere, $P_B = 0{\cdot}1$ atmosphere (at 15° C.), and a certain mixture exerts a total pressure of

0·3 atmosphere, what are the proportions of A and B in the mixture, and what is the affinity of formation of 100 mols. of the mixture from the pure components?

Answer **50** per cent. (molecular of each.)
$A =$ **400 calories.**

$$0{\cdot}3 = x_A \times 0{\cdot}5 + (1 - x_A) \times 0{\cdot}1 \qquad x_A = 0{\cdot}5$$

$$A = RT \times 100 x_A \log \frac{P_A}{p_A} + RT \times 100\,(1 - x_A) \log \frac{P_B}{p_B}$$

$$= 2 \times 288 \times 50 \times 2{\cdot}3 \left(\log \frac{0{\cdot}5}{0{\cdot}25} + \log \frac{0{\cdot}10}{0{\cdot}05}\right)$$

$$= 664 \times 0{\cdot}6021 = 400 \text{ calories.}$$

65. A mixture of C_6H_5Cl ($P_A = 863$) and C_6H_5Br. ($P_B =$ 453) at 136°·7 obeys the linear formula, equation (2), p. 96.

What is the composition of the mixture which will boil at this temperature, under a pressure of 760 millimetres, and what is the ratio of mols. chloro—to mols. bromobenzene in the vapour from mixtures containing (1) 1 per cent. of C_6H_5Cl; (2) 1 per cent. of C_6H_5Br.? In which direction will the composition of the liquid vary, on isothermal distillation of the two mixtures?

Answer **25·01** mols. per cent. of C_6H_5Cl.

$\frac{p_A}{p_B} =$ (1) **6·019**; (2) **188.**

Pure C_6H_5Br will be left in each case.

$\frac{p_A}{p_B}$ throughout $= 1{\cdot}904 \times \left(\frac{x_A}{1-x_A}\right)_L$.

(See Young, "Stoichiometry").

66. Benzene and ethylene dichloride are another pair of liquids which obey equation (2).

At a certain temperature $P\ (C_6H_6) = 268{\cdot}0$ mm. $P\ (C_2H_4Cl_2) = 236{\cdot}2$ mm.

What is the composition of the liquid when the partial pressures of the two components are equal?

Answer **47** mols. per cent. of C_6H_6.

v. Zawidski (*Zeitsch. physikal Chem.* (1900), 35, 129).

67. What physical meaning can be attached to equation (1), p. 96, if the exponent "*a*" is equal to zero?

Answer Since $(r)_V = k$ the partial pressures are independent of $(r)_L$, and this can only be the case if the vapour pressure of A is uninfluenced by that of B, that is to say, the liquids are immiscible.

Similarly, it can be shown by the phase rule, that if the liquids are immiscible, the total vapour pressure of the two is invariable at one temperature. For $f = 2 - 3 + 2 = 1$, and t is arbitrarily fixed.

68. The liquids chlorobenzene and water are practically immiscible:—

t	$P (C_6H_5Cl)$	$P (H_2O)$
90°	208·35	525·45
91	215·8	545·8

Young ("Fractional Distillation").

The boiling point at intermediate pressures may be calculated by the method of proportional parts from the total pressures at 90° and 91°.

What is the boiling point of the mixture, under a pressure of 740·2 mm., and what is the weight composition of the distillate?

Answer **90·23°.**

71 grams per cent. of $\mathbf{C_6H_5Cl}$.

Show how this applies to the practice of steam distillation.

Find the separate partial pressures of the components corresponding to the previously determined boiling point (method of proportional parts), and hence the molecular percentage by the gas laws.

69. For any positive value of "*a*" in equation 1, the total pressure, composition curve will have a maximum:

i.e.: $$\frac{dP}{dx} = \frac{dp_1}{dx} + \frac{dp_2}{dx} = 0 \quad . \quad . \quad . \quad . \quad (1)$$

Lehfeldt (*Phil. Mag.* 1898 [v.] 46, 42).

Show that when this is the case:

$$\frac{x}{p_1} - \frac{1-x}{p_2} = 0 \qquad \therefore (r)_L = (r)_V \quad . \quad . \quad (3)$$

For $$\frac{x}{p_1} \cdot \frac{dp_1}{dx} + \frac{1-x}{p_2} \cdot \frac{dp_2}{dx} = 0 \quad . \quad . \quad . \quad (2)$$

Substituting the value of $\frac{dp_1}{dx}$ from (1):

$$\left(\frac{x}{p_1} - \frac{1-x}{p_2}\right) \frac{dp_2}{dx} = 0$$

and $\frac{dp_2}{dx}$ is not equal to 0.

When the ratios (r) and $(r)_V$ are expressed in grams for C_6H_6 and CCl_4, the following relation holds good:

$$\log (r)_V = 0{\cdot}065 + 0{\cdot}947 \log (r)_L$$

Lehfeldt (*loc. cit.*).

What is the composition corresponding to the constant boiling mixture?

Answer **94·4** per cent. by weight of C_6H_6.

70. Distinguishing the molecular ratios of *A* and *B* in the liquid and vapour phase by:—

$$(r_m)_V \text{ and } (r_m)_L$$

and the ratio of grams by:

$$(r)_V \text{ and } (r)_L,$$

show that if:

$$(r)_V = (r)_L \times K'$$

and $$(r_M)_V = (r_M)^a{}_L \times K,$$

where $K = \frac{P_A}{P_B}$ = the ratio of the vapour pressures of the pure liquids, then

$$K' = K\left(\frac{M_A}{M_B}\right)^{a-1}$$

(M_A and M_B being the respective molecular weights)

and
$$\frac{1}{K} = \frac{1}{K'}\left(\frac{M_A}{M_B}\right)^{1-a}$$

Lehfeldt (*loc. cit.*).

F. D. Brown (*Journ. Chem. Soc.* (1879), 35, 547).

(„ „ (1881), 39, 304).

The composition of the distillate from the mixed liquids C_6H_6 (A) and CS_2 (B) can be represented by:

$$\log (r)_V = 0{\cdot}9 \log (r)_L + \bar{1}{\cdot}48 \left(\text{in which } r = \frac{A}{B}\right)$$

This relation does not alter much between 48° and 77°.

Mixtures containing 95, 50 and 20 per cent. by weight of benzene boil at 76°·2, 55°·7, and 49°·2, respectively.

Find the composition of the distillate from each, the amount of distillate being negligible compared to the amount of boiling liquid; also the ratio between the vapour pressures of the pure liquids

$$\frac{P\,(CS_2)}{P\,(C_6H_6)}.$$

Prove that there is a mixture of maximum vapour pressure, and find its composition.

Answer **81·0, 23·2, 8·0** per cent. of **C_6H_6 in distillate.**

$$\frac{P_{CS_2}}{P_{C_6H_6}} = \mathbf{3{\cdot}32}.$$

There is a maximum, but it is very close to the CS_2 end of the curve, the ratio $\frac{C_6H_6}{CS_2}$ in vapour and liquid being $\mathbf{6{\cdot}31 \times 10^{-6}}$.

71. In the case of ethyl alcohol and ethyl ether at 7·2°, the pressures of the pure liquids are 24·37 and 264·7 mm., respectively (Wüllner).

What are the total pressures of mixtures containing $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{5}$ of their weights of alcohol, and what is the composition of the mixture of minimum boiling point (maximum vapour pressure), if $K = \frac{p_A}{p_B}$ and $a = 0·5$? (See Problem 70.)

Answer **183·0, 213·3, 236·6** mm.
98·6 per cent of ether by weight.

It can be shown that the partial pressures of the components are given by the formula :

$$p_A = \left(\frac{M_B\,(r)_L}{M_B(r)_L + M_A}\right)^a P_A \quad p_B = \left(\frac{M_A}{M_B(r)_L + M_A}\right)^a P_B$$

Lehfeldt (*loc. cit.*)

$19·1 + 163·9 = 183·0.$

At maximum pressure :

$$\log r = 0·5 \log r + \log K'$$

Margules Equation (Introduction, p. 97).

Calling the exponents of e in the equation for p_A and p_B, X_A and X_B respectively, show that at a maximum of total pressure

$$\frac{e^{X_A}}{e^{X_B}} = \frac{P_B}{P_A}$$

and hence $X_A - X_B = 2·303 \log \frac{P_A}{P_B}$

72. Numerous data are to be obtained from the work of v. Zawidski referred to in Problem 66, p. 129.

For ethyl acetate (A) and carbon tetrachloride (B) at 50°, the constants are as follows :

$$a_2 = 0·601 \; a_3 = -\,0·0655$$
$$P_A = 280·5 \; P_B = 307·2$$

What are the partial pressures of each component in a mixture of $x_A = 0{\cdot}6$ mols. of A? And what is the composition of the mixture of minimum boiling point?

Answer $p_A = \mathbf{176{\cdot}4}$ $p_B = \mathbf{136{\cdot}0}$.
0·347 mols. A and **0·653** mols. B.

$$\log p_A = \log P_A + \log x_A + 0{\cdot}4343 \times X_A, \text{ etc.}$$

whence p_A and p_B may be obtained.

At the maximum:

$$\left(\frac{x_A}{1 - x_A}\right)_V = \frac{p_A}{p_B} = \left(\frac{x_A}{1 - x_A}\right)_L$$

i.e., $$\frac{P_A x_A e^{X_A}}{P_B(1 - x_A)e^{X_B}} = \frac{x_A}{1\ x_A}\,\frac{e^{X_A}}{e^{X_B}} = \frac{P_B}{P_A}$$

and $$\frac{a_3 x_A{}^2}{2} - (a_2 + a_3)x_A = 2{\cdot}3026 \times \log\frac{P_B}{P_A} - \frac{a_2}{2} - \frac{a_3}{3}$$

whence x_A may be obtained.

73. The ratio of the weights of O_2 and N_2 in the vapour and liquid phase, at the boiling point of liquid air, under normal pressure, can be expressed by the formula:

$$\log (r)_V = \log a + b \log (r)_L$$

and $a = 0{\cdot}2097$ $b = 1{\cdot}06737$.

Baly (*Phil. Mag.* (1900) [5] 49, 517).

What is the composition of the first portion of the gas collected from liquid air (23 per cent. of O_2)?

A mixture of liquid O_2 and N_2 at 90° absolute gives a vapour containing 89·8 per cent. of O_2, what is the percentage composition of the liquid?

Answer (1) **5·46** per cent. O_2.
(2) **96·15** per cent. O_2.

74. For "ideally concentrated" reactions from room-temperature downwards (see also 10, p. 241) the free energy is very nearly equal to the total energy.

Nernst (*Wied. Ann.* (1894), 53, 57).

Test this statement by calculating the affinity at 15° of the mixing of 1 mol. of water ($p = 12·674$) with a large quantity of 52·13 per cent. aqueous sulphuric acid (p_{H_2O} from this mixture $= 4·215$), and comparing it with the heat effect of the same process, as calculated by Thomson's formula. Problem 19, p. 31.

$$\text{Answer} \quad A = \mathbf{630} \text{ cal.}$$
$$q = \mathbf{695} \text{ ,,}$$

$$A = RT \log \frac{P}{p}. \quad q = \frac{dQx}{dx} \; (x = 5).$$

75. What are the values of A and q for the transference of 1 mol. of water from a mixture 1 $H_2SO_4 + 9·93\ H_2O$ (mols.) to a mixture 1 $H_2SO_4 + 5·89\ H_2O$ (mols.), at 0° C., the pressures of water vapour being 2·952 and 1·679 mm. over the respective acids?

Take $RT \log = 1{,}252$.

The net heat effect of the transference is evidently here, the difference between two differential heats of solution. (See Problem 22, p. 32.)

$$\text{Answer} \quad A = \mathbf{307·1} \text{ calories.}$$

$$q = \frac{dQ_{b_2}}{d_b} - \frac{dQ_{b_1}}{d_b} = \mathbf{310·2} \text{ calories.}$$

76. The ratio of the pressures of water vapour in equilibrium with $BaCl_2 \cdot 2H_2O$ (crystalline) to the pressure in equilibrium with pure water, at the same temperature, are at 18°·5, 0·1905, and at 43°·45, 0·3204.

What is the heat of hydration of $BaCl_2$ per mol. of crystal formed?

Answer + **7,700** calories.

(See equation (2), p. 98.)

Van't Hoff (Lectures, Vol. I.).

77. Calcium chloride hexahydrate can be dehydrated to two different forms (α and β) of the tetrahydrate. The two systems have different vapour pressures, *i.e.*:

$t°$	p, *system* $6 + 4\alpha$	p, *system* $6 + 4\beta$
0	0·092	0·076 mm.
10	0·192	0·162

Roozeboom (*Zeitsch. physikal Chem.* (1889), 4, 43).

What is the heat effect of the transformation $4\alpha \longrightarrow 4\beta$ (mols.)?

Answer **648** calories absorbed.

Consider the vaporisation of 1 mol. of water from the two systems with the formation of 4α and 4β, and the absorption of heat $Q\,(6 \longrightarrow 4\alpha)$ and $Q\,(6 \longrightarrow 4\beta)$. If q are the corresponding amounts of heat absorbed in the condensed reactions: $Q\,(6 \longrightarrow 4\alpha + V) - Q\,(6 \longrightarrow 4\beta + V) = q\,(6 \longrightarrow 4\alpha + L) - q\,(6 \longrightarrow 4\beta 4L)$, since the heat equivalent to work done against external pressure is equal for the two vaporisations.

If $+ q$ is made equal to the heat evolved, the expression becomes:

$$q\,(4\alpha \longrightarrow 6 + L) - q\,(4\beta \longrightarrow 6 + L) = q\,(4\alpha \longrightarrow 4\beta).$$

78. A saturated solution is in osmotic and vapour pressure equilibrium with a crystalline hydrate. No work is done on the whole by removing 1 gram of water from the crystal as vapour, and returning it osmotically as liquid.

Consequently, if p' and p are the pressures in millimetres of saturated water vapour over the crystal and pure water, P, the osmotic pressure in atmospheres, and D_V and D_L, the densities of the water vapour and liquid,

then $d(pV_V) + d(PV_L) = 0 \quad - \dfrac{dp}{dP} = \dfrac{V_L}{V_V} = \dfrac{D_V}{D_L}.$

In the case of water $D_V = p \times 0{\cdot}0_3806 \times \frac{273}{T}$. Hence, show that $- \log p' = \frac{P}{4{\cdot}55T} + Ci$

$$- \log p = Ci.$$

$$P = 10{\cdot}5T \log \frac{p}{p'}.$$

The dissociation pressure of $CuSO_45H_2O + CuSO_4 \,.\, 4H_2O$ is 21·726 mm. at 39°·7 and 2·993 at 14°·0. The vapour pressures of water are 54·06 and 11·87 at these temperatures.

What is the osmotic pressure of the pentahydrate at the two temperatures?

Answer **1,300** atmospheres.
1,800 ,,

Van't Hoff ("Chemical Dynamics").

79. At $t° = 30{\cdot}0$, the osmotic pressure of $ZnSO_4\,7H_2O$ is 532, that of $6H_2O$ is 709 atmospheres. What are the dissociation pressures of the two hydrates, if the vapour pressure of water at 30°·0 is 31·42 millimetres?

Answer **21·38** millimetres.
18·45 ,,

Van't Hoff (*loc. cit.*).

80. The transition temperature T_0 of the above two forms of $ZnSO_4$ hydrate is 39°.

From the data of the preceding problem, determine the heat of formation of the higher hydrate from the lower and water at 29°, assuming that q does not vary widely within 10° of T_0.

Answer + **2,760** calories.

$$ZnSO_4\,7\,H_2O, \log C_0 - \log C = \frac{q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$,, \quad 6\,H_2O, \log C_0 - \log C' = \frac{q'}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

q, q' being the inner heats of vaporisation (evolved).

Therefore, if $q - q'$ is found to be negative, the heat of dehydration is negative, and the heat of hydration positive.

Van't Hoff (*loc. cit.*).

81. From the mean value of $q = 2{,}880$ calories, find the affinity of hydration of the lower hydrate at $t = 19°$ and at $t = 59°$.

Answer **+ 185** calories.
— 185 „

$$A = RT \log \frac{C}{C'} = \frac{q}{RT}\left(\frac{T_0 - T}{T_0}\right) RT$$

Note.—In the equations for the heat of vaporisation of water from $ZnSO_4 \cdot 7\,H_2O$ and $ZnSO_4 \cdot 6\,H_2O$, *i.e.*, $\log p_0 - \log p = \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$, the concentration C may be used instead of p, by substituting $p = CRT$. This simply has the effect of adding $\log T_0 - \log T$ to the left-hand side. But since there are two equations to determine $q - q'$ between the same temperature limits this term also cancels, and either C or p may be used in calculating $q - q'$.

Van't Hoff (*loc. cit.*).

82. The difference between the heats of solution of $2KCl + CuCl_2$ and $2KCl \cdot CuCl_2 \cdot 2H_2O$ is $+ 3{,}063$ calories for each half molecule of the double salt. This is equal to the heat of formation of the double salt from the anhydrous salts and water, or to the difference between the heats of vaporisation of water from water and from the hydrate. Hence, determine the dissociation pressure of the hydrate at 92° and at 42° from the following:

t	42°	46°·6	92°
$p\ (2KCl \cdot CuCl_2 \cdot 2H_2O)$		24	
$p\ (H_2O)$	62	77·5	566·7

J. G. C. Vriens (*Zeitsch. physikal Chem.* (1891), 7, 194).

Answer $p' =$ **318·0** mm. at 92°.
18 mm. at 42°.

Van't Hoff (*loc. cit.*).

83. A salt hydrate $AB \cdot CH_2O$ forms a saturated solution, $AB + x\, H_2O$ at temperature T.

Q_{LV} is the heat of vaporisation of pure water (1 mol.); q_{SL}, the heat absorbed on the precipitation of 1 mol. of the hydrate from the saturated solution, and p is the vapour pressure of the saturated solution.

Show that:

$$\frac{d \log p}{dt} = \frac{Q_{LV} + \frac{q_{SL}}{x - c}}{RT_2}$$

The following values of x, q_{SL} refer to a saturated solution of $CaCl_2 . 6\, H_2O$.

The value of Q_{LV} for pure water may be derived from the equation:

$$Q_{LV} = 606{\cdot}5 - 0{\cdot}695t^{\circ}$$

t	p	x	q_{SL}	$\frac{d \log p}{dt}$ *observed.*
0	18	10·37	— 6,900	0·055
10	32	9·49	— 7,175	0·047
20	52	8·28	7,575	0·043
25	62	7·52	7,900	0·026
27	64	7·13	8,100	0·012
28	64·5	6·93	8,250	+
28·5	65	6·81	8,340	± 0
29	64·5	6·67	8,435	—
29·5	64	6·46	8,550	—
30	61	6·00	— 8,900	∞

Calculate the values of Q, the total heat absorbed per mol. of the hexahydrate precipitated (see below), at $t = 0^{\circ}$, $28{\cdot}5^{\circ}$ and 30°.

Plot the values of $\frac{Q}{x - c}$ for 1 mol. of water against t, and compare the graph with the corresponding graph for pure water.

Find the value of $\frac{d \log p}{dt}$ (natural logs.) at $t = 10°, 28°, 29°, 29°{\cdot}5$ and $30°$.

$$Q \text{ (for 1 mol. of salt precipitated)} = (x - c)\, Q_{LV} + q_{SL}$$

$$Q \text{ (for 1 mol. of water evaporated)} = Q_{LV} + \frac{q_{SL}}{x - c}.$$

Answer $Q = + \mathbf{40{,}807}$ at 0°.
$+ \mathbf{210}$ at 28°·5.
$- \mathbf{8{,}900}$ at 30°.

$$\frac{d \log p}{dt} = \mathbf{0{\cdot}0545,\ 0{\cdot}0094,\ -\ 0{\cdot}012,\ -\ 0{\cdot}045,\ \infty}$$

Roozeboom (*Zeitsch. physikal Chem.* (1889), 4, 31).

GAS REACTIONS (HOMOGENEOUS).

Let A_1, A_2, A_1', A_2', etc., be the different species of reacting molecules. A dash indicates that the molecules are on the resultant side of the equation.

$n_1\ n_2$, $n_1'\ n_2'$ are the coefficients of the stoichiometrical equation :

$$n_1 A_1 + n_2 A_2 \ldots = n_1' A_1' + n_2' A_2' \ldots$$

Let N_1, N_1', etc., be the actual number of molecules of each species present in the equilibrium quantity of reacting mixture. $N = N_1 + N_2 \ldots + N_1' + N_2' \ldots =$ the total number of molecules present at any moment.

w_1, w_1', etc. = the weights of each molecular species.

M_1, M_1', etc. = the molecular weights of each species.

$$N_1 = \frac{w_1}{M_1}, \text{ etc.}$$

Let p_1, p_1', etc., be the corresponding partial pressures.

Then $p = \frac{NRT}{v} = \frac{(N_1 + N_2 \,.\,.\, + N_1' + N_2' \,.\,.) \;\; RT}{v}$

$$= C_1 + C_2 \,.\,.\, C_1' + C_2' \,.\,.\,) \, RT = CRT$$

$$p_1 = \frac{N_1RT}{v} = C_1RT, \text{ etc.} \quad . \quad . \quad . \quad . \quad (1)$$

$$p_1 = \frac{N_1\,p}{N}, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$k_p = \frac{p_1^{\,n_1} \,.\,.}{p_1'^{\,n_1'} \,.\,.} = \frac{(C_1^{\,n_1} \,.\,.\,)RT^{\Sigma n}}{(C_1'^{\,n'_1} \,.\,.\,)RT^{\Sigma n'}} \quad . \quad . \quad . \quad (3)$$

$$\text{Also, } Kp = \frac{(N_1^{\,n_1} \,.\,.\,)\,p^{\Sigma n} \times N^{\Sigma n'}}{(N_1'^{\,n_1'} \,.\,)\,p^{\,\Sigma n'} \times N^{\Sigma n}} \quad . \quad . \quad . \quad (4)$$

Or, if the summation (Σ) is made over the whole of the coefficients (n_1, etc.) of the stoichiometrical equation (n_1, etc., being called positive and n_2, etc., negative),

$$\log Kp = \Sigma n \log p \qquad \log Kc = \Sigma n \log C \quad . \quad (5)$$

$$Kp = \frac{(N_1^{\,n_1} \,.\,.\,)\,p^{\,\Sigma n}}{(N_1'^{\,n_1'} \,.\,)N^{\,\Sigma n}}, K_c = \frac{N_1^{\,n_1} \times N_2^{\,n_2}}{N_1'^{\,n_1'} \times N_2'^{\,n_2'}\,V^{\Sigma n}} \quad (6)$$

But $\frac{p}{N} = \frac{RT}{v}$

$$\therefore Kp \, \frac{(N_1^{\,n_1}\,.)(RT)^{\Sigma n}}{(N_1'^{\,n_1'} \cdot)\,v^{\Sigma n}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\text{and } \frac{Kp}{(RT)^{\Sigma n}} = \frac{(N_1^{\,n_1}\,.)}{(N_1'^{\,n_1'}\,.)v^{\Sigma n}} = \frac{(N_1^{\,n_1}\,.\,)\,p^{\,\Sigma n}}{(N_1'^{\,n_1'}\,.\,)(RT)^{\Sigma n}} = K_c \quad (8)$$

$$\log Kp = \log K_c + \Sigma n \log R + \Sigma n \log R + \Sigma n \log T \quad (9)$$

The maximum work which a given reaction is capable of affording is the work which is done by the system when it is made to pass isothermally and reversibly from a given initial to a given final state.

This can be proved by the laws of thermodynamics, and illustrated by a mechanism similar to that used to calculate the work of expansion of a perfect gas (see pp. 48, 89).

The reacting gases, A_1, A_2, etc. of equation (1) above, at the arbitrary partial pressures, P_1, P_2, etc., are combined to form the resulting gases A_1', A_2', etc., at the arbitrary partial pressures P_1', P_2', etc., through an equilibrium box in which all the gases are present at the equilibrium partial pressures $p_1, p_2 \,.\,.\, p_1', p_2' \,.\,.$

$$\left.\begin{aligned}\text{Maximum Work} &= \Sigma n\, RT \log P - \Sigma n\, RT \log p \\ &= \Sigma n\, RT \log P - RT \log Kp\end{aligned}\right\} \quad (10)$$

the reactants being taken as positive in the summation.

This expression consists of a variable term $\Sigma n\, RT \log P$, and an invariable term $RT \log Kp$.

It is sometimes convenient to fix our ideas by considering the maximum work done by the combination of one stoichiometrical set of reactants $n_1 A_1 + n_2 A_2$ etc., all at atmospheric pressure, to produce one set of resultants $n_1' A_1' + n_2' A_2'$ etc., all at atmospheric pressure. In this case the first term vanishes, and the maximum work is numerically equal to $RT \log Kp$.

The affinity of a reaction at any temperature is defined as the maximum work, when one stoichiometrical set of reactants is combined to form one stoichiometrical set of resultants at constant volume (see Donnan, "Thermodynamics").

Therefore,

$$\text{Affinity} = \Sigma n\, RT \log C - RT \log K_c,$$

or, substituting pressures for concentrations,

$$\text{Affinity} = \Sigma n\, RT \log P - RT \log K_p \,. \qquad . \quad (10a)$$

By aid of the preceding conceptions, the driving force of a chemical reaction can be expressed in the same way as that of a gas expansion or change of state, such as vaporisation. Consequently, the applications of the second law of thermodynamics, developed in the preceding sections are available also for the quantitative treatment of chemical energetics.

The change of the equilibrium constant with temperature may be expressed by an equation, similar in form to those of Clausius and Clapeyron :

$$\frac{d \log K_c}{dt} \text{ (reactants +)} = \frac{q}{RT^2} \quad . \quad . \quad . \quad (11)$$

$$\text{Hence } \log K_c = -\frac{q}{RT} + C_i \text{ (integration constant)} \quad (12)$$

$$\log K_2 - \log K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \quad . \quad . \quad (13)$$

These integrations have been carried out on the assumption that q does not vary much over the temperature interval considered.

Suppose that T_1 and T_2 are widely different from one another, or that q varies rapidly with T ("Thermochemistry," pp. 18, 20, 21, equations (2), (12), (10a).

$$\text{then } \frac{dq}{dt} = \Sigma n \, H_v$$

$$H_v = a + 2\,b'T + 3\,c'T^2$$

$$q - q_0 = \Sigma naT + \Sigma nb'T^2 + \Sigma nc'T^3$$

$$\log K_c = -\frac{q_0}{RT} + \frac{\Sigma na}{R} \log T + \frac{\Sigma nb'T}{R} \;. \; . \; C_i \quad . \quad (14)$$

$$\log K_p = -\frac{q_0}{RT} + \frac{\Sigma n\,(a + R)}{R} \log T + \frac{\Sigma nb'T}{R} + C_i + \Sigma n \log R \quad . \quad . \quad . \quad (15)$$

(See equation (9), p. 141.)

The constant $(C_i + \Sigma n \log R)$ can, as Nernst has shown, be replaced by $\Sigma n\,(C_i + \log R)$. The separate $C_i + \log R$ were obtained from the characteristic equations for the vaporisation of each of the pure substances present (components of the system), and may be called the chemical constants (C_i) for each substance (see Nernst, "Thermodynamics and Chemistry," pp. 53—76).

A generalisation with regard to the specific heats of gases at low temperatures allows the equation to be reduced to a form suitable for calculations (see "Thermochemistry," Problems 45, 46, p. 41).

$$\log Kp = -\frac{q_0}{4{\cdot}57\ T} + \Sigma n\ 1{\cdot}75\ \log T + \frac{\Sigma nb'}{4{\cdot}571} T + \Sigma n C_i \quad . \quad . \quad . \quad . \quad (16)$$

$\Sigma nb'$ referring to the alterations of the mean specific heats with temperature, as above.

GAS REACTIONS (HETEROGENEOUS).

The separate phases of a reacting system may be :—

A. Phases of variable composition, such as mixtures of gases and solutions of variable concentration.

B. Phases of constant composition, such as pure solids, which are miscible only in the form of vapour or solute.

A. If the system consists of two or more phases of variable composition, and if C_1, C_2, are the concentrations of the reacting molecules in phase I, and C'_1, C'_2 the concentrations of the reacting molecules in phase II,

$$\text{then } C_1 = K_1 C'_1 \quad C_2 = K_2 C'_2$$

(see "Equilibrium in Solution," p. 180) where K_1, K_2 are the constant distribution ratios of the molecules between the phases.

The equilibrium constants of the reaction in the separate phases are :

$$K_c = \frac{C_1^{\,n} \times C_2^{\,n_2}}{C_1^{\,\prime n_1'} \times C_2^{\,\prime n_2'}} \text{ and } K_c' = \frac{(K_1 C'_1)^{n_1}}{(K_2 C'_2)^{n_2}}$$

$$\therefore \log K'_c = \log K_c + \Sigma n \log K \quad . \quad . \quad (1)$$

That is, if the equilibrium constant of a reaction in a single phase and the distribution ratios of the reacting molecules between this and a second phase are both known, then, the equilibrium constant of the reaction in the second phase can also be deduced.

B. If there are several phases of constant composition S_1, S_2 present, the concentrations C_{s_1}, C_{s_2}; C'_{s_1}, C'_{s_2}, etc., of the corresponding molecules in all the phases of variable composition are also constant.

$$K_c = \frac{C_1^{n'} \times C_2^{n_2} \cdots C_{S_1} \times C_{S_2}}{C_1'^{n'_1} \times C_2'^{n'_2} \cdots C'_{S_1} \times C'_{S_2}} \quad . \quad (2)$$

C_{s_1}, etc., being constant, their values can be taken into the equilibrium constant and

$$K'_c = \frac{C_1^{n_1} \times C_2^{n_2}}{C_1'^{n'_1} \times C_2'^{n'_2}} . \quad . \quad . \quad (3)$$

This equation has the same form as that of a homogeneous equilibrium, those molecular species alone being included which are not in equilibrium with pure condensed phases.

If all the concentrations C_1 are saturation concentrations C_{s_1}, there can be no incomplete equilibrium such as prevails in a homogeneous reacting system.

Thus, although at one particular temperature solid Hg, S and HgS might exist side by side (*i.e* when $p_{Hg} \times p_s = Kp_{HgS}$ and therefore the affinity of combination $= 0$); yet, this is not an incomplete but a complete equilibrium in the gas phase, since neither temperature nor concentration can be altered without the complete disappearance of one phase.

This is a system of three components in four phases, therefore invariant and possessing no degree of freedom. At all other temperatures Hg and S will tend to pass completely over into HgS, or vice versa.

The above is sometimes called the law of incompatibility of condensed systems, a law which is also exemplified by the existence of melting points and transition temperatures systems of one component.

As already stated in the case of homogeneous equilibrium (see p. 143).

$$\frac{d \log Kc}{dT} = \frac{q}{RT^2} \text{ (reactants positive)}$$

$$\frac{d \log Kp}{dT} = \frac{Q}{RT^2} \text{ (reactants positive)}$$

q and Q are the amounts of heat evolved by the combination reactants → resultants at constant volume and pressure, and K_c and K_p contain the resultants in the numerator.

Suppose first that the integration is carried out over a small interval of temperature, within which q remains practically constant,

$$\text{then } \log K_2 - \log K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ as before.}$$

If the reaction is a combination of dissociation products in the stoichiometrical proportions n_1, n_2 to form an undissociated solid,

$$\text{then} \quad K_c = C_1^{n_1} \times C_2^{n_2} \cdot \cdot \cdot = \frac{p_1^{n_1} \times p_2^{n_2}}{(RT)^{n_1 + n_2}}$$

$$p_1 = \frac{PN_1}{N_1 + N_2} \text{ etc.} \quad \text{(} P \text{ referring now to the total pressure of the system.)}$$

$$= n_1 \log N_1 \ldots\ldots - n'_1 \log N'_1$$
$$+ \Sigma n \log P - \Sigma n \log RT \quad . \quad . \quad . \quad (4)$$

If the reaction is carried out at two temperatures T_1 and T_2,

$$\log K_1 - \log K_2 = \Sigma (n_1 \log N_1) - \Sigma (n_2 \log N_2) +$$
$$\Sigma (n_1 \log P_1) - \Sigma (n_2 \log P_2) - \Sigma (n_1 \log N_1RT_1) +$$
$$\Sigma (n_2 \log RT_2) \quad . \quad . \quad . \quad (5)$$

the suffixes $_1$ and $_2$ referring now, not to the various molecular species at one temperature, but to the whole of the molecules at the two temperatures T_1 and T_2.

In the particular case of the binary dissociation of a solid,

$$(n_1 + n_2 \ldots) \log \left(\frac{P_2}{T_2} - \log \frac{P_1}{T_1}\right) = \frac{q}{R}\left(\frac{T_2 - T_1}{T_1\,T_2}\right) . \quad (6)$$

Suppose now that it is necessary to take into account the variation of the heat of reaction with temperature.

q, the heat evolved by the total reaction in this case includes:—

$\Sigma n\lambda$ = the heat absorbed by the production of the saturation concentrations of the reactants from the condensed forms; λ_1, λ_2 etc., being the inner heats of vaporisation of each.

q' = the heat evolved by the reaction in the phase of variable composition.

$\Sigma n'\lambda'$ = the heat evolved by the condensation of the resultants.

Applying Nernst's method of obtaining the thermodynamic integration constant (p. 143) (Nernst, "Thermodynamics and Chemistry," p. 96):

$$\log K_p = -\frac{q_0}{RT} + \Sigma n\, 1{\cdot}75 \log T + \frac{\Sigma nb + \Sigma n_S b_S T}{4{\cdot}571} + \Sigma n C_i \quad . \quad . \quad . \quad . \quad (7)$$

The suffix $_S$ signifies that the molecules are present also as phases of constant composition; *e.g.*, $\Sigma n_S b_S$ refers to the alteration of the specific heats of condensed phases with temperature.

These coefficients are, generally speaking, not known with sufficient accuracy, but being in most cases small may frequently be omitted. The result is a simplified formula with a theoretical basis, which in many cases gives a good agreement with experiment.

$$\log K_p = -\frac{q_o}{4{\cdot}571T} + 1{\cdot}75 \log T + \Sigma n C_i \quad . \quad (8)$$

The quantities q, 1·75, etc. refer, as before, to 1 gram molecule, and q is conveniently taken as the heat of reaction, at room temperature.

Homogeneous Equilibrium.

1. One gram molecule of a gas is found to occupy a volume of 40 litres at $T = 400°$.

If the degree of dissociation according to the equation $AB \rightleftarrows A + B$ is known to be 2 per cent., find the total pressure, Kp and Kc ($p_A \cdot p_B = K_p \cdot p_{AB}$).

$$n_A = 0{\cdot}02 = n_B\,;\ n_{AB} = 0{\cdot}98\,;\ N = 1{\cdot}02\,;$$

$$pv = NRT = 1{\cdot}02 \times {\cdot}0821 \times 400 \text{ litre atmospheres};$$

$$P = \mathbf{0{\cdot}829} \text{ atm.}$$

$$K_p = \frac{(0{\cdot}02)^2\,P^2}{(1{\cdot}02)^2} \times \frac{1{\cdot}02}{P \times 0{\cdot}98} = \frac{00_34 \times {\cdot}829}{1{\cdot}0}\,;$$

$$Kc = \frac{C_A C_B}{C_{AB}} = \left(\frac{{\cdot}02}{40}\right)^2 \times \frac{40}{0{\cdot}98}\,.$$

$$\text{Also } K_c = \frac{K_p}{RT^{\Sigma n}} = \frac{K_p}{RT}\,.$$

Answer $K_p = \mathbf{0{\cdot}0_3\,3316}$.

$K_c = \mathbf{0{\cdot}0_41}$.

2. The degree of dissociation of 1 original mol. of HI at 450° C., and 1 atmosphere is 0·2198 (Bodenstein *Zeits. phys. Chem.* (1897), 22, 1). Calculate the dissociation constants K_p and K_c. Also show that the degree of dissociation is unaffected by the change of volume, and find the partial pressure of I_2 when the volume of the equilibrium mixture is doubled.

If a = the fraction of 1 mol. dissociated, it gives $\frac{a}{2}$ mols. of H_2 and I_2, and leaves $1 - a$ of HI.

$$K_p = \frac{(0{\cdot}2198)^2}{4({\cdot}7802)^2} \qquad K_p = K_c = \mathbf{{\cdot}01984} \quad \text{Answer} \quad . \quad (1)$$

$$p_{I_2} = \frac{N_{I_2}}{N} \cdot P = \frac{a \times 0{\cdot}5}{2 \times 1} \text{ for } \begin{cases} \dfrac{P}{P_1} = \dfrac{NRT}{V} \cdot \dfrac{V_1}{N_1RT} \\ V_1 = 2V \quad N = N_1 \\ \therefore P = 2P_1. \end{cases}$$

$$p_{I_2} = \mathbf{{\cdot}0549} \quad \text{Answer} \quad . \quad . \quad . \quad (2)$$

3. Find the partial pressures of H_2, I_2, and HI in an equilibrium mixture derived from original HI at 445° C. and at a total pressure of 76 mm.

Answer $p = \mathbf{8{\cdot}36}$ mm.

4. In an experiment of von Falckenstein (*Zeits. phys. Chem.* (1909), 68, 277) a mixture of HI and its dissociation products at 1108° C., and a total pressure of 164·7 mm. was found to contain H_2 at a partial pressure of 2·9 mm. (by means of a platinum bulb originally evacuated and permeable to H_2 at this temperature). Find the percentage dissociation of 1 original mol. of HI and the equilibrium pressure in atmospheres.

$$a_{H_2} = \frac{2p_{H_2}}{P}$$

Percentage dissociation = **0·758** Answer.

$K_p = \mathbf{1{\cdot}46 \times 10^4}$ Answer.

5. If the constant K_c for the reaction :

$$2SO_2 + O_2 = 2SO_3 \text{ at } 900° \text{ is } 3{\cdot}16 \times 10^{-4},$$

what is the value of the constant K_p at the same temperature?

Answer **0·74.**

6. Deduce a formula for the relation between x = gram molecules of HI formed from a reacting mixture of 1 mol. of H_2 with " a " of I_2, and the equilibrium constant K.

$$\text{Answer} \quad x = \frac{-1 - a\sqrt{a^2 + 2a + 1 + 4a(4K - 1)}}{2(4K - 1)}$$

(See Problem 1, above.)

Van't Hoff (" Lectures on Theoretical and Physical Chemistry ").

7. 20·57 centigram molecules of H_2 are mixed with 5·22 I_2, and allowed to react at a temperature at which $K = 0{\cdot}02$ $\left(\frac{[H_2] \times [I_2]}{[HI]^2}\right)$. Find the number of centigram molecules of HI formed.

Answer HI = **10** centigram molecules.

Van't Hoff (*loc. cit.*).

8. How many molecules of I_2 must be added to a reacting mixture (derived from 1 original mol. of HI) at 445°, in order to reduce the degree of dissociation from 21·98 to 10 per cent.?

$$\frac{\left(a + \frac{0{\cdot}1}{2}\right)(0{\cdot}1)}{2(1 - 0{\cdot}1)^2} = 0{\cdot}0198.$$

Answer I_2 added = **0·271** mols.

9. A compound A_1 dissociates into A_1' and A_2'. According to the equation:

$$A_1 = 2A_1' + 3A'_2$$

The percentage dissociation, at 400° absolute and a total pressure of 0·8 atmosphere is 25. Find the volume occupied, and the equilibrium constant, K_p (reactants in numerator).

$$V = \frac{NRT}{p} = \{1 + (\Sigma n' - 1)\,a\}\,\frac{RT}{p}\cdot$$

Answer **82·1** litres

$Kp =$ **1059.**

(See equation (4), Introduction, p. 141.)

$$Kp = \frac{(1 - a)\; p^{\Sigma n - \Sigma n'}}{(n_1'a)^{n_1'} \times (n'_2a)^{n_2'} \times \{1 + (n_1' + n_2' - 1)\,a\}^{\Sigma n - \Sigma n'}}$$

10. If a is the degree of dissociation of N_2O_4 at $t°$ C., and P atmospheres, and D_1 is its relative density under these conditions, deduce formulæ by means of which a and K_p may be found from D_1, and D the theoretical density of N_2O_4 undissociated (=3·181).

At $P = 497{\cdot}75$ millimetres, and $t° = 49°{\cdot}7$, the density of the N_2O_4, NO_2 mixture was 2·144.

Find a and K_p.

$$\frac{D}{D_1} = \frac{1 + a}{1} \quad K_p = \frac{4\,a^2 p}{1 - a^2} = \frac{4p(D - D_1)^2}{(2D_1 - D)\,D}\cdot$$

Answer $a =$ **0·485**

Kp (atm.) = **0·800.**

11. At what pressure (mm. Hg) is the mixture 50 per cent. dissociated?

Answer **456** mm.

12. By the measurements of Natanson (*Wiedemann Annalen der Physik* 24,465 and 27,613) the degree of dissociation of N_2O_4 at $P = 59{\cdot}7$ is 0·483; at $P = 617{\cdot}6$ is 0·174 ($t° = 21{\cdot}5°$ C.).

Compare the values of K_p at the two pressures, and hence, find the volume occupied by 1 original mol. of N_2O_4 at the latter pressure. Also the volume and pressure of the same quantity, when a has been reduced to 0·1 by compression.

Answer. The mean value of K_p is **0·094.**

$$V = \frac{(1 + a)RT}{P} = \mathbf{34{\cdot}92} \text{ litres.}$$

$$P = \mathbf{23{\cdot}25} \text{ atmospheres.}$$

$$V = \mathbf{1{\cdot}144} \text{ litres.}$$

13. When a mixture of HCl and O_2 is passed over a catalyser, the following reaction occurs:

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O.$$

If the initial gas mixture is dry, and x mols. of HCl are transformed at equilibrium out of every 1 mol. taken, prove that:

$$\frac{Cl_2}{HCl} = \frac{x}{2(1 - x)}$$

also that
$$\frac{H_2O}{Cl_2} = 1.$$

By introducing these two relations into the equation:

$$K_p = \frac{\overset{\frac{1}{2}}{p_{H_2O}} \times \overset{\frac{1}{2}}{p_{Cl_2}}}{\overset{\frac{1}{4}}{p_{O_2}} \times p_{HCl}}$$

prove that
$$K_p = \frac{x}{2(1 - x)} \times \frac{1}{p^{\frac{1}{4}}{}_{O_2}}$$

A mixture containing initially 49 per cent. of HCl, and 51 per cent. of O_2 by volume was caused to react at $P = 723$ mm. and $t = 480°$ C. The fraction x of HCl transformed was 0·76.

What is the value of the equilibrium constant K_p (p in atmospheres)?

Answer $K_p = 1{\cdot}9$.

14. Calculate the partial pressure of the oxygen in the above equilibrium mixture.

Can the total number of mols. of equilibrium mixture (derived from pure HCl and O_2 as before) be expressed in terms of the mols. transformed (x), and the mols. of HCl and O_2 originally present?

15. In another experiment at the same temperature, and $p = 720$ mm., 73 per cent. of an original volume of HCl (34·1 c.c.) was transformed at equilibrium. If $K_p = 2{\cdot}0$, find the initial volume of oxygen.

Answer **15·9** c.c.

Haber ("Thermodynamics of Technical Gas Reactions," p. 181).

16. A mixture of SO_2, O_2 and N_2 in the molecular proportions 2·62 : 1 : 3·76 was passed through a silica tube at 1,001° absolute (Bodenstein und Pohl, *Zeitsch. Elektrochem.* (1905), 2, 273). The resulting equilibrium mixture rapidly cooled was found to contain:

$$SO_2 : SO_3 : O_2 = 33{\cdot}9 : 17{\cdot}5 : 10{\cdot}9 \text{ mols.}$$

$P = 759$ mm. throughout.

Find the equilibrium constant K_c, and an expression for the percentage yield $\frac{SO_2 \times 100}{SO_3}$ which would be obtained if N_2 were absent from the mixture of O_2 and SO_2 in the above ratio. The combination is effected at 760 mm.

Note—The amount of nitrogen associated with the resultant mixture must be found and included in the total number of molecules (N) (see equation (6) p. 141).

$$K_c = \frac{N^2{}_{SO_2} \times N_{O_2}}{N_{SO_3}} \times \left(\frac{P}{NRT}\right)^{2+1-2}$$

To find the amount x of O_2 transformed, if there is no

N_2, equate the product $2{\cdot}62 - 2x$ etc., to the found value of K_c.

$$K_c = \frac{(33{\cdot}9)^2 \times 10{\cdot}9}{(17{\cdot}5)^2} \times \frac{1}{136{\cdot}05} \times \frac{759}{760} \times \frac{273}{1{,}001} \times \frac{1}{22{\cdot}42}$$

$$= \mathbf{3{\cdot}65 \times 10^{-3}} \quad \text{Answer.}$$

$$\frac{(2{\cdot}62 - 2x)^2 (1 - x)^2}{(2x)^2} \cdot \frac{1}{3{\cdot}62 - x} \times \frac{273}{1{,}001 \times 22{\cdot}42}$$

$$= 3{\cdot}65 \times 10^{-3} \quad \text{Answer.}$$

17. From the above value of the equilibrium constant K_c, find the numerical value of K_p in Haber's notation (see Problem 13, p. 151).

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \; p^{\frac{1}{2}}_{O_2}}$$

(In what units must R be expressed ?)

If x = fractional yield $\left(\frac{SO_3}{SO_2 + SO_3,}\right)$, show that $x = \frac{1\,Kp\,\sqrt{p_{O_2}}}{1 + Kp\,\sqrt{p_{O_2}}}$ Hence define the conditions for maximum yield and calculate the maximum yield, using O_2 and air (1) at 1,001° and (2) at the temperature at which $Kp = 100$ (see Problem 16, above).

$$Kp = \sqrt{\frac{1}{3{\cdot}65 \times 10^{-3} \times 0{\cdot}0821 \times 1{,}001}} = \mathbf{1{,}825}$$

Answer Maximum yield (1) = **·681** and **·480.**
Maximum yield (2) = **·99** and **·974,**
Haber (*loc. cit.* on p. 152).

Note.—This maximum, based on the utilisation of as much SO_2 as possible does not, of course, represent the optimum for technical practice. Why not? It affords, however, a useful method of seeing which is the most favourable temperature, etc., at a glance: since the percentage yields, under the limiting condition of pure oxygen, may be rapidly calculated, and plotted against temperatures.

18. The degree of dissociation of water vapour has been determined by Nernst and Von Wartenburg (*Zeits. physikal Chem.* (1906), 56, 548). A mixture of steam, with some hydrogen and oxygen, was passed through a heated porcelain tube, and cooled rapidly: the water was measured, and the residual H_2 and O_2 analysed by explosion.

The dissociation being small, the denominator of the equilibrium constant

$$Kp = \frac{p^2_{H_2} \times p_{O_2}}{p^2_{H_2O}}$$

is itself practically constant.

In one experiment at 1,207° C., the residual gases measured 0·6645 c.c. (*N.T.P.*) and completely condensed to water after explosion.

The water collected measured 1·66 c.c.

What is the percentage dissociation at that temperature?

The volume of H_2O dissociated is equal to the volume of H_2 produced. This is equal to:

$$\frac{2}{3} \times 0{\cdot}6645 \times \frac{1{,}480}{273}$$

The volume of steam producing this hydrogen is equal to:

$$\frac{1{\cdot}66}{18} \times \frac{22{,}400}{1} \times \frac{1{,}480}{273}.$$

Therefore, the percentage dissociation is:

$$\frac{\frac{2}{3} \times \frac{{\cdot}6645}{1} \times 100}{1{\cdot}66 \times 1{,}242} = \mathbf{0{\cdot}0188}$$

19. In another experiment, 0·281 c.c. of mixed gases and 2·15 c.c. of liquid water were collected. After explosion, there remained 0·06 c.c. of hydrogen.

The gases were all measured at 20° and 743 mm.

What is the percentage dissociation at the temperature employed 1,124° C.

Answer **0·0073** per cent.

20. In the case of the fractional dissociation of H_2O, show that the equilibrium constant Kc

$$= \frac{P}{RT} \frac{x_1^3}{(2 + x_1)(1 - x_1)^2},$$

where P = pressure in atmospheres and x_1 = fractional dissociation under these conditions.

At $T = 1{,}000°$ and $P = 1$ atmosphere, steam is dissociated to $3{\cdot}00 \times 10^{-5}$ per cent.

What is the percentage dissociation at 10·00; 0·10; and 0·01 atmosphere?

$3 \log 100x_1 = 3 \log 100x - 1$ (for 10 atmospheres).

Answer $100x \times 10^5 =$ **1·39 ; 6·46 ; 13·9**

21. Show that the equilibrium constant K_1 of the reaction : $CO + H_2O = CO_2 + H_2$ is equal to :

$$\sqrt{\frac{K_2}{K_3}},$$

where K_2 refers to the reaction :

$$2\,CO + O_2 = 2\,CO_2,$$

and K_3 to the reaction :

$$2\,H_2 + O_2 = 2\,H_2O.$$

Hence, if the fractional dissociation of CO_2 at 1,300° is $0{\cdot}0_4\,407$, and of H_2O is $0{\cdot}0_4\,266$, find the equilibrium constant K_1, and the quantities of gases resulting from a mixture of 1 mol. each of CO and H_2O, at this temperature, the pressure being 1 atmosphere throughout.

Answer $K_1 =$ **2·673**

$$\frac{(1 - x)^2}{x^2} = 2{\cdot}673 \qquad 1{\cdot}673\,x^2 + 2\,x - 1 = 0.$$

Answer **·38** mols. of the CO and H_2O are transformed.

22. Hahn has found the equilibrium constant of the water gas equilibrium K_1 in last problem to be 1·70 at 1300°.

From this, and the dissociation of H_2O at that temperature = 0·00291, find the percentage dissociation of CO_2.

If x_2 is the degree of dissociation of the CO_2, and x_3, that of the H_2O,

$$\frac{[CO]^2 \times [O_2]}{[CO_2]} = \frac{[x_2]^2 \times \left[\frac{x_2}{2}\right]}{[1 - x_2]^2 v_2} = K_2$$

There is a similar equation for the dissociation of the H_2O.

Also $1 - x_2$ and $1 - x_3$ are nearly equal to 1.

$$\therefore v_2 = NRT = v_3.$$

and

$$\frac{[CO]^2\ [H_2O]^2}{[CO_2]^2\ [H_2]^2} = K_1^2.$$

Hence, deduce the required relation between x_2, x_3, and K_1.

Answer $100\ x\ (CO_2) =$ **0·00414.**

23. The following relation between Kp, heat of reaction, temperature and specific heats has been calculated by Von Falckenstein.

$$\log \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}} = \frac{25{,}010}{T} - 2{\cdot}42 \log T + 1{\cdot}43 \times 10^{-4}T + 0{\cdot}683 \times 10^{-7}T^2 + 1{\cdot}896$$

$$\text{and } \log \frac{p^2_{H_2} \times p^2_{Cl_2}}{p^4_{HCl}} = \frac{-\ 88{,}000}{4{\cdot}571\ T} + 0{\cdot}284 \log T - 0{\cdot}001\ T - 1{\cdot}6.$$

What is the degree of dissociation of HCl at 1,829° and 1 atmosphere ?

Answer **0·21** per cent.

What is the equilibrium constant of the Deacon process at $t = 450°$ and at $t = 600°$?

$$\log K_p = \frac{p^2_{Cl_2} \times p^2_{H_2O}}{p_{O_2} \times p^4_{HCl}}\ .$$

Answer $K =$ **36·4**

$K =$ **0·959.**

(Compare Problem 13, p. 151).

24. Show that the numerical value of the affinity of a reaction is independent of the pressure units of K_p, and is the same whether K_p or K_c is used; and that the units in which the result is expressed depend simply on the unit of the gas constant R.

(Introduction, equation (10a), p. 142).

25. Given that CO_2 is 0·003 per cent. dissociated at 1,000° C., find the maximum work obtainable from the combination $2\ CO + O_2 = 2\ CO_2$ at this temperature, the reactant and resultant non-equilibrium mixtures each having a total pressure equal to 1 atmosphere, the reactants being mixed in the stoichiometrical proportions ($R = 2$).

$$A = RT\ \Sigma n \log p - RT \log \frac{(0_4 3)^2\,(0_4 15)}{1}$$

$$= 80{,}900 \text{ cal. for 1 mol. of } CO_2.$$

26. If oxygen is passed through carbon at 1,000° the equilibrium mixture is finally found to contain 99·3 per cent. of CO, and 0·7 per cent. of CO_2. Find the partial pressure of the O_2 present, from the data of the last equation, the total pressure being 1 atmosphere. The equilibrium constant 1 must hold in the presence of carbon, since the same three gases are present, and the partial pressure of solid carbon may be taken as constant.

(Equations (2), (3), p. 145.)

Answer $p_{O_2} = 6{\cdot}71 \times 10^{-19}$

Weigert, Kohlenstoff (Abegg, "Handbuch").

27. From the preceding, find the maximum work obtainable when oxygen at atmospheric pressure and 1,000° C. is isothermally combined with carbon, to form CO_2.

$$A = RT \log \frac{1}{p_{O_2}} - RT \log \frac{1}{p_{CO_2}}$$

For the process may be carried out reversibly by pressing

1 mol. of O_2 into the equilibrium box, and removing 1 mol. of CO_2.

Answer $A = \mathbf{93,207}$ calories.

28. From the equality of A and q at the absolute zero, the heat of combustion :

$$C + O_2 = CO_2 + 97,650 \text{ calories at } 0^\circ \text{ C.}$$

and the approximate equality in the heat capacities of $C + O_2$ and CO_2, deduce a general formula for the alteration of A with T (see preceding Problem).

Answer $A = \mathbf{97650 - 3{\cdot}49}\ T$.

29. Also calculate the maximum work for the combustion of 1 mol. of O_2, at a pressure of 1 atmosphere, to (1) CO_2; (2) $2CO$ at 1,050° C.

The percentages of CO and CO_2 in the equilibrium mixture $C + CO_2 + CO + O_2$ at 1,050° were 0.34 and 99·66 respectively (Boudouard).

Answer A (for $C + O_2 \longrightarrow CO_2$) $= \mathbf{119,000}$ cal.
(for $2\ C + O_2 \longrightarrow 2\ CO$) $= \mathbf{88,900}$ cal.

The equilibrium constant of the reaction : $2\ CO + O_2 \longrightarrow 2\ CO_2$ may be calculated from the degree of dissociation x given by the Nernst formula (Problems 40, p. 163 ; 44, p. 40 ; 20, p. 155 ; and equation (15), p. 143) (Nernst, " Thermodynamics and Chemistry, p. 81) :

$$3 \log x = -\frac{29,600}{T} + 1{\cdot}75 \times \log T - 0_366 \times T + 3{\cdot}9$$

$$x = N_{CO} \qquad \frac{x}{2} = N_{O_2} \text{ from 1 mol. of } CO_2.$$

The equilibrium constant so found is equated to the product of the partial pressures in the carbon and oxides reaction, and hence the unknown p_{O_2} in this mixture is found. The maximum work is then obtained by combining 1 mol. of oxygen to the partial pressure prevailing in the equilibrium box and removing 1 mol. of CO_2 or 2 mols. of CO respectively.

30. The affinity of the reaction:

$$2\ CO + O_2 = 2\ CO_2$$

has been calculated by Haber and Moser, from the results of Nernst and Von Wartenburg.

$$A = 134{,}880 - 11{\cdot}14\ T \log T + 0{\cdot}0034\ T^2 - 11{\cdot}9\ T + RT \log \frac{p^2_{CO}\ \ p_{O_2}}{p^2_{CO_2}}.$$

From this and the preceding data (Problem 29, above), calculate the affinity of oxidations of $2C$ to 2 CO by O_2, at 500° C. previously establishing a formula connecting A with T.

$$\begin{array}{c} 2\ C + 2\ O_2 = 2\ CO_2 + 2\ A_3 \\ 2\ CO + O_2 = 2\ CO_2 + A_1 \\ \hline 2\ C + O_2 = 2\ CO + 2\ A_3 - A_1\ (= A_4) \end{array}$$

Answer $A_4 = 60{,}420 + 11{\cdot}14\ T \log T - 0{\cdot}0034\ T^2 + 4{\cdot}9\ T + RT \log \frac{p_{O_2}}{p_{CO}}$

A_4 at 500° C. = **87,080.**

31. Calculate the affinities of the three reactions for 17°, 500°, 1,000°, 1,250° and 1,500° C., and plot the values of A against T.

See Weigert in Abegg, "Handbuch," III., 2, for a full discussion of these results.

At what temperature will the affinities of the three oxidations (1 mol. of O_2 in each case) be equal?

Answer **690°**

32. The reduction of a metal oxide by carbon (*i.e*,, the oxidation of carbon by combined oxygen) ought to furnish the same maximum work, whether the oxygen is combined directly with C to form CO_2, or, with the intermediate formation of CO.

Prove that this is the case, by determining the affinities

($\Sigma n \log P = O$) of the direct and indirect oxidations, at 500° and 1,000°.

$$\text{Answer}\quad \left.\begin{array}{ll}\text{at } 500^\circ & \mathbf{94{,}940}\text{ cal.}\\ \text{at } 1{,}000^\circ & \mathbf{93{,}190}\text{ ,,}\end{array}\right\}\text{ in both cases.}$$

33. It is desired to reduce a metallic oxide at 500° and at 1,000°. If we choose the reducing agents according to their affinity of oxidation, which is preferable, other things being equal: C (to CO) or CO (to CO_2), at 500° and 1,000°.

Answer CO to CO_2 at **500°**.
C to CO at **1000°**.

34. The affinity of the reaction $2H_2 + O_2 = 2H_2O$ is given by the formula :

$$A = 114{,}400 - 7{\cdot}6\ T \log T + 0{\cdot}0025T^2 - 4{\cdot}68T$$
$$+ RT \log \frac{p^2{}_{H_2} p_{O_2}}{p^2{}_{H_2O}}$$

And that of the $CO + O_2$ reaction, by the formula in Problem 30, p. 159; find the affinity for the CO, steam, reaction :

$$2CO + 2H_2O = 2CO_2 + 2H_2$$

Answer $A = \mathbf{20{,}480} - 3{\cdot}54T \log T + 0{\cdot}0_39T^2 - 7{\cdot}22T$

$$+ RT \log \frac{p^2{}_{CO} \times p^2{}_{H_2O}}{p^2{}_{CO_2} \times p^2{}_{H_2}}$$

35. At what temperature can mixtures of equal volumes of CO and H_2O; and of CO_2 and H_2 be mixed together without any reaction; in other words,—what is the temperature corresponding to an equilibrium mixture containing equal volumes of the four gases?

The required temperature is most easily found by solving the equation for various values of T, and plotting A against T.

Answer $T = \mathbf{930}$

(See Weigert, *loc. cit.*, Problem 26.)

36. The equilibrium constant $K_c \dfrac{\text{reactants}}{\text{resultants}}$ for the reaction $2SO_2 + O_2 = 2SO_3$ is $1{\cdot}55 \times 10^{-5}$ at 801°; $7{\cdot}55 \times 10^{-5}$ at 852°, and $3{\cdot}16 \times 10^{-4}$ at 900° absolute.

Find the heat evolved by the reaction per mol. of SO_3 by means of equation (13), p. 143.

Answer $q = 42{,}055$ and $45{,}390$ for $2\ SO_3$
Mean q for $1\ SO_3 =$ **21,900**

What is the heat of the reaction, if carried out at constant pressure?

Bodenstein and Pohl (*loc. cit.*, Problem 16, p. 152).

37. The densities of N_2O_4, NO_2 mixture are 2·65 and 1·65, at 26·7° and 111·3° respectively.

What is the heat of dissociation of 1 mol. of N_2O_4 at constant volume (see Problem 10, p. 150)?

$\dfrac{d \log K_c}{dt} = + \dfrac{q}{RT^2}$ (if $K = \dfrac{\text{reactants}}{\text{resultants}}$ and $q =$ the heat evolved by the dissociation)

$$\log \frac{4\,a^2{}_2}{(1 - a_2)v_2} - \log \frac{4\,a^2{}_1}{(1 - a_1)v_1} = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and $$p = 1,\ v_2 = N_2RT_2 = (1 + a_2)RT_2$$

$$q = (\log \frac{4\,a^2{}_2}{1 - a^2} - \log \frac{4\,a^2{}_1}{1 - a_1{}^2} + \log T - \log T_1)\frac{4{\cdot}57T_1T_2}{T_2 - T_1}$$

Answer q (for dissociation) $= -$ **12,900** cal.

38. Compare the affinity $\left(- RT \log K_c \dfrac{\text{reactants}}{\text{resultants}}\right)$ with the heat effect of the reaction:

$$H_2 + I_2 = 2HI$$

if the equilibrium constant K_c above is 0·02 at 445°, and 0·015 at 360°.

Answer $A = +$ **5,590** cal. at 445°.
$q = +$ **3,050** cal. between 360° and 445°.

39. Compare the affinities (see problem 38) of the reaction:

$$2SO_2 + O_2 = 2SO_3$$

at 801° and 900° absolute (Problem 36, above).

$$\text{Answer} \quad \frac{A(801^\circ)}{A(900^\circ)} = 1{\cdot}31.$$

40. The following example from Nernst ("Theoretische Chemie") will serve to illustrate the method of calculating gas equilibria, at different temperatures from thermal data.

The relation between q and T for the reaction:

$$2\,CO + O_2 = 2\,CO_2$$

has been found from the specific heat data (see "Thermo-Chemistry," Problem 44, p. 40).

$$q = 135{,}400 + 3{\cdot}83\,T - 0{\cdot}00588\,T^2 + 1{\cdot}47 \times 10^{-6}T^3$$

$$\text{But } \log K_p = \int\frac{qdt}{RT_2} + \int\frac{aTdt}{RT^2} + \int\frac{b'T^2dt}{RT^2} + \int\frac{c'T^3dt}{RT^2} + \Sigma n \log T + \Sigma n C_i$$

a, b' and c' being the coefficients of increase of the mean specific heats (see equation (15), p. 143).

Introducing the log factor:

$$\log K_p = -\frac{135{,}400}{4{\cdot}571T} + \frac{3{\cdot}83 + 1{\cdot}985}{1{\cdot}985}\log T - \frac{{\cdot}00588\,T}{4{\cdot}571} + \frac{1{\cdot}47 \times 10^{-6}}{4{\cdot}571 \times 2}T^2 + \Sigma n C_i$$

$$= -\frac{29{,}600}{T} + 2{\cdot}93 \log T - 001286T + 1{\cdot}61 \times 10^{-7}T^2 + \Sigma n C_i.$$

The quantities of heat referring to 2 mol. of CO_2 formed.

$$\text{But } \log K_p = \log \frac{N_1^{n_1} \times N_2^{n_2} \ldots P^{\Sigma n}}{N'^{n'_1}_1 \times N'^{n'_2}_2 \ldots N^{\Sigma n}}.$$

If x is the degree of dissociation of CO_2 at equilibrium,

$$2CO + O_2 \rightleftarrows 2CO_2.$$

Mols. of each $= x, \frac{x}{2}, \quad 1 - x.$ Total mols. $= 1 + \frac{x}{2}$ (N)

,, ,, $= 2x, x, 2(1 - x)$,, ,, $= 2 + x$

$$\text{and } \log K_p = \log \frac{(4x^2 \times x)(2+x)^2}{4(1-x)^2(2+x)^3} = \log \frac{x^3P}{(2+x)(1-x)^2}$$

$$\therefore \log K_p - \log K_{po} = -\frac{q_o}{2{\cdot}3R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{a+R}{R}\log\frac{T}{T_o}$$

$$+ \frac{b}{2{\cdot}3R}(T - T_o) + \frac{c}{2 \times 2{\cdot}3R}(T^2 - T_o^2)$$

$$\textit{i.e.,}\ \log \frac{x^3P}{(2+x)(1-x)} - \log \frac{x_o^3P}{(2+x_o)(1-x_o)}$$

$$= \log K_p - \log K_{po}.$$

Now, since $P_o = 1$, x_o is small compared to 2 or 1;

$$\therefore (2 + x_o)(1 - x_o) = 2$$

and, x_o at 1,000° absolute $= 1{\cdot}58 \times 10^{-5}$ per cent.

Then, $\log (100x_o)^3P = -14{\cdot}404$;

also $$\frac{q_o}{2{\cdot}3RT_o} = \frac{29{,}600}{1{,}000} = 29{\cdot}60$$

$$\therefore \log 2(100x)^3 + \log \frac{P}{P_o} = 15{\cdot}20 - \frac{29{,}600}{T} + 2{\cdot}93 \log \frac{T}{1{,}000}$$

$$- 0{\cdot}001286(T - 1{,}000) + 1{\cdot}61 \times 10^{-7}(T^2 - 1{,}000^2)$$

At what temperature will CO_2 be ·978 and 4·88 per cent. dissociated at $P = 1$ atmosphere? Find the values of x corresponding to round values of T, plot on squared paper, and obtain x by interpolation.

Answer **1,900°** and **2,200°** absolute.

41. In the case of the reaction:

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

$$q = 114{,}400 + 2{\cdot}74T - 0{\cdot}0_363T^2 - 6{\cdot}24 \times 10^{-7}T^3.$$

At 1,000° absolute and $P = 1$ atmosphere, the percentage dissociation was found to be $3{\cdot}02 \times 10^{-5}$. Find the number of cubic centimetres of H_2 and O_2 in a litre of steam at $T = 2{,}000°$, and at $P = 1$ and 10 atmospheres.

Answer **5·92** and **2·73** c.c. of H_2 measured under the above conditions.

Proceed exactly as in the previous case of the $2\,CO + O_2$

$= 2\ CO_2$ reaction, and obtain the corresponding formula for the percentage dissociation at any temperature.

$$\log \frac{(100x)^3}{(2+x)(1-x)} + \log \frac{2P}{P_o} = 11{\cdot}46 - \frac{25{,}030}{T} + 2{\cdot}38 \log \frac{T}{1{,}000} - 1{\cdot}38 \times 10^{-4}(T - 1{,}000) - 0{\cdot}685 \times 10^{-7}(T^2 - 1{,}000^2)$$

in which $P_o = 1$.

Now if $P = 1$ and x is small, $3 \log x$ may be equated to the right-hand side.

And the degree of dissociation at any other pressure P' is given by the equation :

$$3 \log x + \log P = 3 \log x' + \log P'.$$

42. When the dissociation is far reaching, it is no longer permissible to put $(2 + x)(1 - x) = 2$. Thus, at a pressure of 0·1 atmosphere and $T = 2{,}500$, what is the percentage dissociation of H_2O and CO_2?

Answer **8·16** and **30·7** per cent.

Nernst ("Theoretische Chemie.")

43. What is the integration constant I or ΣnC_i from the preceding data, for the formation of $2H_2O$ at 1,000° abs.?

Answer **— 1·76.**

$$\log K_p = \log \frac{x_o{}^3 P}{2} = -\frac{25{,}030}{1{,}000}, \text{ etc. } \ldots + \Sigma nC_i.$$

44. The specific heat data of Problem 46, p. 41, and a value of $\Sigma nC_i = -0{\cdot}2$ for the reaction :

$$2H_2 + O_2 = 2H_2O$$

allow the temperature to be calculated at which water-vapour is dissociated to the extent of 0·0189 and 0·199 per cent.

The observed temperatures are 1,480° and 1,800°.

First derive the equation :

$$\log K_p = \log \frac{x^3}{2} = -\frac{Q_o}{4{\cdot}571T}, \text{ etc.}$$

(See equation (16), p. 144.)

Solve for several values of T and plot the x thus obtained against T.

Answer $T =$ **1,455°** and **1,745°**.

Nernst ("Thermodynamics and Chemistry").

45. From the specific heat data of Problem 47, p. 41, obtain an expression for the value of log K_p at various temperatures (Introduction, p. 147).

$$H_2 + HgO = H_2O + Hg.$$

Answer

$$\log K_p = \frac{47{,}520}{4{\cdot}571T} - 1{\cdot}75 \log T + 0{\cdot}0_37T + \Sigma nC_i \frac{\text{reactants}}{\text{resultants}}.$$

Nernst (*loc. cit.*, p. 42).

46. In view of the present lack of exact data concerning specific heats, the approximation formula (16), p. 144, allows of many calculations of great utility.

The heats of a number of binary dissociations have been calculated by Brill (*Zeitsch. physikal. Chem.* (1907), 57, 721).

For the dissociation:

$$N_2O_4 \rightleftarrows 2NO_2$$

$$K_p = \frac{1 - a^2}{4a^2P} \frac{\text{reactants}}{\text{resultants}}$$

(See Problem 10, p. 150.)

Hence, and from the Nernst formula referred to above, find the value of the heat of dissociation between the temperatures given below, and from the average value of $q = -12{,}400$ cal., calculate the term ΣnC_i at $P = 1$.

Density of $N_2O_4(D_o) = 3{\cdot}1789$ (air $= 1$):

T	D
299·7	2·65
384·3	1·65

Answer $q =$ **− 12,350.** $\Sigma nC_i =$ **− 3·470.**

47. From the results of a number of vapour-density determinations, of which the mean temperature was 509° absolute, Gibbs ("Thermodynamic Studies") has derived the following formula connecting the observed density D with temperature and pressure (in millimetres) for acetic acid:

$$\log \frac{2{\cdot}073(D - 2{\cdot}073)}{(4{\cdot}146 - D)^2} = \frac{3{,}520}{T} + \log P_{mm} - 11{\cdot}349,$$

4·146 (Do) being the density (air = 1) of the double molecules $(CH_3COOH)_2$.

Find the relation between the expression on the left-hand side and K_p, and calculate the value of q and ΣnC_i:

$$\log K_p = \log \frac{1 - a^2}{4a^2P} = \log \frac{D_o(2D - D_o)}{(D_o - D)^2}$$

Hence, as in the last problem:

$$\log \frac{D_o(2D - D_o)}{(D_o - D)^2} = \frac{q}{4{\cdot}571T} - 1{\cdot}75 \log T + \log P_{atm} + \log 4 + \Sigma nC_i.$$

Also, $\log \dfrac{D_o(2D - D_o)}{(D_o - D)^2} = \dfrac{3{,}520}{T} + \log P_{atm.} + \log 4 - 11{\cdot}349$

Answer $q = -$ **16,090** $\Sigma nC_i = -$ **3·73.**

48. By a determination of density the temperature at which $C_5H_{10}\ HBr$ is one half dissociated was found to be 525° at atmospheric pressure. $\Sigma n = 1$ and C_i, for most substances is in the neighbourhood of 3. Hence, find the heat of dissociation (per mol).

$$\log \frac{1 - a^2}{a^2P} = \log 3 \text{ when } a = 0{\cdot}5 \text{ and } P = 1.$$

Answer $q =$ **19,400.**

49. Find the temperature at which this compound is one half dissociated at $P = 0{\cdot}1$ atmosphere.

Answer **470°.**

Heterogeneous Equilibrium.

50. Iron decomposes steam, forming an oxide and hydrogen. The reaction has been investigated by Deville, and more recently by Preuner (*Zeitsch. physikal. Chem.* (1904), 47, 385).

The mixture of iron and oxide was kept at a high temperature (900°), and the cooler part contained water at a known temperature. The total pressure $H_2 + H_2O$ was read on a manometer as follows :

$P\ (H_2O)$	P
10·0	24·2
49·3	121·1

Assuming the reaction to take place according to the equation :

$$3\,Fe + 4H_2O = Fe_3\,O_4 + 4H_2$$

find the value of the reaction constant at this temperature, and hence the maximum percentage yield of H_2, when steam at atmospheric pressure is passed over iron at 900°.

Answer $K_p = (0{\cdot}69)^4$.
59·2 per cent. of H_2.
(Equation (3), p. 145).

51. The constants at 900°, 1,025°, and 1,150° are 0·69, 0·78, and 0·86 for the reaction :

$$FeO + H_2 = Fe + H_2O.$$

If the pressure of water-vapour was constantly 10 mm., what is the increase of total pressure when the $Fe + FeO$ is heated to 1,125°, no H_2 being present at the beginning ?

Answer **11·6** mm. of mercury (due to the formation of H_2).

52. The constant of the reaction :

$$FeO + H_2 = Fe + H_2O$$

is 0·57 at 1,000° absolute. At this temperature water-vapour is dissociated to $3{\cdot}0 \times 10^{-5}$ per cent. What is the affinity of combination ($-RT \log p_{O_2}$) between oxygen at atmospheric pressure and iron at this temperature, and what is the dissociation pressure of oxygen over the oxide formed?

Answer **46,500** cal. $P_{O_2} = \mathbf{4 \times 10^{-21}}$ atm.

$$FeO + H_2 = Fe + H_2O + A_1 \qquad A_1 = RT \log (K_p)_1 \frac{\text{resultants}}{\text{reactants}}$$

$$\frac{H_2 + \frac{1}{2} O_2 = H_2O + A_2}{FeO = Fe + \frac{1}{2} O_2 + A_1 - A_2} \qquad A_2 = RT \log (K_p)_2 \frac{\text{resultants}}{\text{reactants}},$$

$$\therefore A_3 = A_1 - A_2 = RT \{\log (K_p)_1 + \log (K_p)_2\} = -\log p_{O_2}$$

53. Ammonium hydrosulphide is completely dissociated with H_2S and NH_3, when vaporised (Van't Hoff, Cohen (Ewan), "Studies in Chemical Dynamics," p. 156), (Isambert, Compt. rend. 1881 and 1882).

If the dissociation pressure of the solid is 175 mm. at 9·5°, and 501 mm. at 25·1°, what is the molecular latent heat of vaporisation at constant pressure and at constant volume, the temperature being 17·3° (Clausius equation)?

Answer **21,390** and **22,545** calories absorbed.

Since there are 2 mols. of gas formed from each mol. of NH_5S, the external work of vaporisation corresponds to $2RT$ calories.

54. From the data of Problem 51, p. 167, calculate the heat Q evolved by the reaction:

$$FeO + H_2 = Fe + H_2O, \text{ at } 960° \text{ C.}$$

Answer — **2,968** calories.

Use the Clausius equation

$$\frac{d \log K_p}{dt} (H_2O \longrightarrow H_2) = \frac{Q}{RT^2} \text{ evolved } (H_2O \longrightarrow H_2).$$

How does this compare with the heat of reduction of $\frac{1}{3}$ Fe_3O_4 calculated from the specific heat data of Problem 48, p. 42 (Thermochem.).

Answer — **2,970** as against — **2,650** calories.

If the iron were really present as FeO, how would this affect the thermochemical calculations in the problem referred to?

55. Show that equation (8), p. 147, accounts for the constancy of $\frac{Q}{T}$ at the boiling point (Le Chatelier, Forcrand) in the case of substances yielding the same gaseous product of dissociation.

From the heat (+ 42,520) of the reaction:

$$CaO + CO_2 = CaCO_3$$

calculate the temperature at which the dissociation pressure of $CaCO_3$ is equal to 1 atmosphere, and compare it with the temperature calculated from $\frac{Q}{T} = 33$.

$$C_i \text{ for } CO_2 = 3{\cdot}2.$$

Answer **1,098** as against **1,290°**.

56. What will be the partial pressure of CO_2 in equilibrium with $CaCO_3$, at room temperature, say 300° absolute?

Answer $p = \mathbf{2 \times 10^{-24}}$ atmosphere.

(See preceding problem.)

57. The heat of combination Q of gaseous NH_3 and H_2S to form solid NH_5S (1 mol.) is + 22,800 calories, at $T = 300°$. At this temperature the specific heats are:—

$$NH_5S = 19{\cdot}1 \quad NH_3 = 9{\cdot}5 \quad H_2S = 8{\cdot}5.$$

The chemical constants of NH_3 and H_2S are 3·3 and 3.0.

Calculate the temperature corresponding to a dissociation pressure $p = 0{\cdot}661$ atmosphere by means of equations (7) and (8), p. 147.

Answer $T =$ **318** by equation (7).
$=$ **312** ,, ,, (8).

The term $\Sigma\ (nb' + n_S b'_S)$ is first calculated as in Problem 47, p. 41, and from it the values of q_O, etc., are found.

Note that the terms q_0, etc., originally obtained with the above quantities of materials correspond to 2 mols. of gas, whereas K_p, etc., in the equations (7) and (8) are stated on the assumption that 1 mol. of gas is condensed or vaporised.

58. Show that in the case of a binary dissociation yielding a gas with the chemical constant 3·0 (which is about the average) the quotient $\frac{Q}{T}$ is 29·7 when the boiling point is 100°; 33·6 when it is 300°; 35·3 when it is 500°; and 37·7 when it is 1,000°.

59. $PbCO_3$ gives off its CO_2 with a rush (boils) at $t°$ C. = 302 and $P = 1$ atmosphere (Colson). Find the heat of combination for each mol. of $PbCO_3$.

Answer $q = \mathbf{21{,}110}$.

60. It is known that the dissociation temperatures of $CaCl_2\ 4NH_3$ and $2AgCl\ 3NH_3$ lie between 300° and 500°. Using the value of $\frac{q}{T}$ for a mean temperature of 400 (see Problem 58 above), calculate to a first approximation the values of T from the heats of dissociation — 10,290 and — 11,580 calories.

What will be the ammonia pressure over the $CaCl_2$ compound at $T = 300°$?

(Take chemical constants = 3·0 throughout.)

Answer $T = \mathbf{298°{\cdot}2}$ and $\mathbf{335°{\cdot}9}$

$P = \mathbf{513{\cdot}9}$ mm.

$$\frac{q}{T} = \frac{33{\cdot}6 + 35{\cdot}3}{2} = 34{\cdot}5$$

For other examples, see Nernst (" Thermodynamics and Chemistry ").

REACTIONS IN SOLUTION.

The equilibria between reacting molecules in a condensed system (such as an aqueous or non-aqueous solution) are governed by the laws already stated for gas equilibra.

As in the case of gases, the regularities are most clearly traceable in systems dilute with respect to the reacting molecules. For, just as the simple gas laws cease to hold at high concentrations, so the laws of solution equilibrium depart more widely from simplicity as the concentration increases. In the latter case there is the additional complication due to the rapid variation of the influence of the solvent, an influence which must, of course, be great at any time, but may be imagined more constant in the case of dilute solutions.

With these reservations, the laws of equilibrium may be at once applied to many important cases. Since the changes of volume are usually small, the distinction between reactions at constant pressure and those at constant volume can often for practical purposes and in a preliminary treatment of the subject be ignored.

The fact that one or more of the molecular species reacting in aqueous solution are electrically charged has given to investigators a method which has been successfully used in the important field of electrolytic aqueous solutions. It is with such solutions that the following section is chiefly concerned.

The symbols and units employed have been defined with some detail, since exact definitions and a consistent use of the electrochemical units is here of particular importance.

Reactions in Solution (Homogeneous).

Definitions.

η = Concentration in equivalents per cubic centimetre.

$C = 1{,}000\ \eta$. Concentration in equivalents per litre.

κ = Specific conductivity. Current passing through 1 square centimetre of an electrolyte, 1 centimetre in thickness, under the potential gradient of 1 volt per centimetre, or current density under unit potential gradient. If the current density is expressed in amperes per square centimetre, and the potential gradient in volts per centimetre, then the conductivity is in mhos per centimetre cube.

F = 96,540 coulombs. Coulombs required to deposit 1 gram equivalent at each electrode.

Λ = Equivalent conductivity. Conductance of so much solution as contains 1 gram equivalent, when in the form of a plate 1 centimetre thick, the opposite sides being electrodes.

In other words, the equivalent conductivity is equal to the specific conductivity divided by the gram equivalents per cubic centimetre (η), or multiplied by the dilution or cubic centimetres per gram equivalent (v)

$\Lambda = \kappa v = \frac{\kappa}{\eta}$ or, if C = equivalents per litre and V = litres per equivalent.

$$\Lambda = \kappa V 1{,}000 = \frac{\kappa 1{,}000}{C}.$$

The molecular conductivity μ is defined as above, substituting gram molecules for gram equivalents.

$\mu = n_A n_K \Lambda$ (where n_A, n_K refer to the valencies of the anion and kation).

The total current Λ carried by 1 gram equivalent under unit potential gradient as above, is proportional to :

(1) The charge on each gram ion = F coulombs.

(2) The number of electrically free gram equivalents $= 2\,a$ (where a is the degree of dissociation).

(3) The absolute velocity of each ion $(U_A + U_K)$.

Therefore $\Lambda = 96{,}540\,a\,(U_A + U_K)$ . . . (1)

TABLE OF RELATIONS BETWEEN UNITS.

	Total	*Anion*	*Kation*
Absolute Velocities .	$U_A + U_K$	U_A	U_K
Apparent Velocities .	$a\,(U_A + U_K)$	$aU_A,\ U_A$	$aU_K,\ U_K$
Limiting Conductivity (Equivalent and Ionic)	$F\,(U_A + U_K)$ Λ_o	FU_A L_A	FU_K L_K
Equivalent and Ionic . Conductivity for each Concentration . .	$Fa\,(U_A + U_K)$ $\Lambda,\ a\Lambda_o$	FaU_A $aL_A,\ l_A$	FaU_K $aL_A,\ l_K$
Specific Conductivity . At Concentration η .	$\eta Fa\,(U_A + U_K)$ or $\eta\Lambda,\ a\eta\Lambda_o$	$\eta l_A,\ \eta a L_A$	$\eta l_K,\ CaL_K$

With the litre as unit of volume $\kappa = \frac{C\Lambda}{1{,}000} \quad \frac{\Lambda}{1{,}000\,V}$.

Single Electrolytes.

An equilibrium must exist between the electrically charged products of dissociation (ions) and the electrically neutral undissociated part of an electrolyte in aqueous solution.

In the case of dilute solutions of slightly dissociated electrolytes, such as the majority of organic acids and bases, an equilibrium constant may be calculated which represents accurately the relation between the total concentration and the degree of dissociation.

Thus, if the total molecular concentration is C, the degree of dissociation a and the volume of the system $V\left(=\frac{1}{C}\right)$.

$(aC)^n = K\,(1 - a)\,C$ by the law of mass action . (2)

In the case of a binary compound of univalent elements:

$$K = \frac{a^2 C}{1-a} = \frac{a^2}{(1-a)\,V} \qquad . \quad . \quad . \quad . \quad . \quad (3)$$

If the degree of dissociation is small, as in the case of weak acids and bases:

$$K = \alpha^2 C,\ \alpha = \sqrt{\frac{K}{C}},\ \alpha C = \sqrt{KC} \quad . \quad . \quad . \quad (4)$$

The number of effective molecules i from 1 gram mol. of an electrolyte which dissociates into n ions is given by the equation:

$$i = 1 + (n - 1)\,\alpha \quad . \quad . \quad (5)$$

If the degree of dissociation is large, as in the case of strong acids and bases, α becomes nearly equal to 1, and $i = n$, *i.e.*, 1 gram mol. of an electrolyte, such as $CaCl_2$ in very dilute solution will behave osmotically as 3 mols.

Mixtures of Electrolytes.

Abegg (Ahrens Sammlung VIII.) Lunden, *ibid.* XIV.

Binary Electrolytes with a Common Ion ($H^{\cdot}$).

Let V_1, V_2 be the volumes of solution containing the two acids.

Before mixing for each acid:

$$K_1 = \frac{H^{\cdot}_1}{V_1} \times \frac{A'_1}{V_1} \times \frac{V_1}{H^{\cdot}_1 A'_1} \qquad K_2 = \frac{H^{\cdot}_2}{V_2} \times \frac{A'_2}{V_2} \times \frac{V_2}{H^{\cdot}_2 A'_2}$$

After mixing:

$$K_1 = \frac{H^{\cdot}_1 + H^{\cdot}_2}{V_1 + V_2} \times \frac{A_1}{V_1 + V_2} \times \frac{V_1 + V_2}{H^{\cdot}_1\, A_1} \quad . \quad . \quad (6)$$

i.e., the concentrations of A and HA are altered in the same ratio by mixing. K therefore retains its former value without an alteration in the degree of dissociation, on the condition that:

$$\frac{H'_1 + H_2}{V_1 + V_2} = \frac{H'_1}{V_1} \left(i.e. \frac{H'_1}{V_1} = \frac{H'_2}{V_2} \right).$$

Two electrolytes can be mixed without a change in their degree of dissociation, if the concentration of the common ion is the same in each.

Or, if a_1 is unchanged after mixing:

$$K_1 = \frac{a_1{}^2}{(1 - a_1)V_1} = \frac{a_1(a_1 + a_2)}{(1 - a_1)(V_1 + V_2)} \quad . \quad . \quad . \quad (7)$$

$$\therefore \frac{a_1}{a_1 + a_2} = \frac{V_1}{V_1 + V_2} \quad \frac{a_1}{V_1} = \frac{a_2}{V_2} \quad . \quad . \quad . \quad . \quad (8)$$

If the dissociation constants K_1 and K_2 of two acids are known, it is possible to find the concentrations which can be mixed without the alteration of a_1 and a_2.

From the preceding, $a_1\,C_1 = a_2\,C_2$ is the required condition.

$$K_1 = \frac{(a_1C_1)^2}{(1 - a_1)C_1} \qquad K_2 = \frac{(a_2C_2)^2}{(1 - a_2)C_2} \quad . \quad . \quad . \quad (9)$$

If K_1 and K_2 are small, $1 - a_1$ and $1 - a_2$ are to a good approximation equal to 1;

$$\therefore K_1\,C_1 = K_2\,C_2,\ \frac{K_1}{K_2} = \frac{C_1}{C_2} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Suppose that the concentrations are such that the degrees of dissociation β_1, β_2, which each acid would have if it alone occupied the volume of the mixture, are altered to a_1, a_2 by their mutual effect upon one another.

Then for acid (1) (and equally of course for (2)):

$$K_1 = \frac{\beta_1\,C_1}{1 - \beta_1} = \frac{a_1(a_1C_1 + a_2C_2)}{1 - a_1} \quad . \quad . \quad . \quad . \quad (11)$$

Since the concentration of the common ion in the mixture $= a_1\,C_1 + a_2C_2$.

Writing a similar equation for K_2 and dividing:

$$\frac{K_1}{K_2} = \frac{a_1}{1 - a_1} \times \frac{1 - a_2}{a_2} = \frac{a_1}{a_2} \text{ (if } K_1 \text{ and } K_2 \text{ are small)}$$

$$\text{Substituting in (1)} \ \frac{\beta_1{}^2C_1}{1 - \beta_1} = \frac{a_1{}^2C_1}{1 - a_1}\left(1 + \frac{K_2}{K_1} \cdot \frac{C_2}{C_1}\right)$$

$$\frac{\beta_1}{a_1} = \sqrt{1 + \frac{K_2}{K_1} \cdot \frac{C_2}{C_1}} \quad . \quad . \quad . \quad (12)$$

Conductivity of a Mixture.

If the electrolytes are all fully dissociated before and after mixture, and if V_1, V_2 are the volumes mixed :

$$\kappa_m = \frac{\kappa_1 V_1 + \kappa_2 V_2}{V_1 + V_2} \quad . \quad . \quad (13)$$

If the solutions are isohydric as above, then the total conductance (= conductivity × volume) of the solution is equal to the sum of the conductances of the components. Then $\kappa_m (V_1 + V_2) = \kappa_1 V_1 + \kappa_2 V_2$ as before.

If the solutions are not isohydric, the value of a, the degree of dissociation of each component in the mixture must first be calculated from K and C (Equation (2) above).

Hydrolysis.

In a solution of salt BA (supposed completely dissociated), there are the ions $B^{\cdot}$, A', $H^{\cdot}$, OH'.

If $K_A \left(= \frac{H \times A}{HA}\right)$ or $K_B \left(= \frac{OH \times B}{BOH}\right)$ or both are small, the concentration of $H^{\cdot}$ or OH' (or both) in pure water may be sufficient to require a considerable equilibrium concentration of HA or BOH (or both). Let the fraction of 1 mol. of salt so decomposed be h.

Then by the law of mass action :

$$(hC)^2 = (1 - h)CK_h \qquad K_h = \text{hydrolysis constant.}$$

Let a_B, a_A, and a_S be the degrees of dissociation of the strong base, strong acid and the salt.

(1) For the salt of weak acid :

$HA = hC$, since the weak acid is practically all undissociated.

$$[OH'] = a_B hC,$$

and

$$[A'] = a_S(1 - h)C ;$$

$$\therefore \quad K_A = \frac{K_w(1 - h)ca_S}{(hc)(a_B hc)} = \frac{(1 - h)a_S}{a_B h^2 c} \quad . \quad (14)$$

(2) Similarly for the weak base:

$$BOH = hc \qquad [H^{\cdot}] = a_A hc \qquad [B^{\cdot}] = a_S(1 - h)c,$$

and
$$K_B = \frac{K_w \times (1 - h)ca_S}{(hc)\,(a_A hc)} = \frac{(1 - h)a_S}{a_A h^2 c} \quad . \qquad (15)$$

(3) For a weak acid and base:

$$BOH = HA = hc,$$
$$B^{\cdot} = A' = a_S(1 - h)c,$$
$$K_A \times K_B = \frac{[H^{\cdot}] \times [A'] \times [OH'] \times [B^{\cdot}]}{[HA] \times [BOH]}$$
$$= \frac{K_w \{a_S(1 - h)c\}^2}{(hc)^2} \quad . \quad . \qquad (16)$$

a_A, a_B, a_S in moderately dilute solutions are all nearly equal to 1. Since the acid, base and salt referred to are highly dissociated,

$$\frac{h^2c}{(1 - h)} = K_h = \frac{K_w}{K_A} \;(14) \qquad = \frac{K_w}{K_B}\,,\,. \qquad (17)$$

and
$$\frac{h^2c^2}{(1 - h)^2c^2} = K_h = \frac{K_w}{K_A \times K_B} \quad . \qquad (18)$$

If the degrees of hydrolysis are only slight, then $1 - h$ is nearly equal to 1,

and $h\sqrt{c} = \sqrt{\dfrac{K_w}{K_B}}$ or $\sqrt{\dfrac{K_w}{K_A}}$ $\qquad h = \sqrt{\dfrac{K_h}{C}}$. (19)

Show that the degree of hydrolysis of a salt of weak acid and base is independent of dilution.

Migration Ratio.

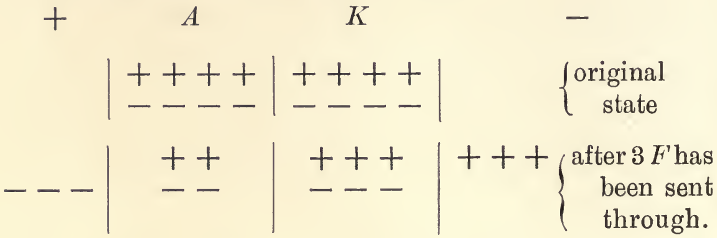
When a current passes through an electrolyte, the fraction carried by each ion (transport number or migration ratio) may be called v_A (anion) and v_K (kation).

Then
$$v_A = \frac{u_A}{u_A + u_K} = \frac{U_A}{U_A + U_K}\,, \text{ etc.} \qquad (20)$$

The migration ratio of anion or kation (according to convenience) may be determined from the total change of concentration in the anode or cathode compartment of the cell.

The sketch below shows the state of a cell with ionic migration, before and after the passage of 3 F.

Each gram equivalent of anion (positive) and kation (negative) on the outside of the electrodes is represented as having been discharged as solid or gas.



In the above case:

$$\frac{\text{Loss of kation from } A}{\text{Loss of anion from } K} = \frac{\text{loss of salt from } A}{\text{loss of salt from } K} = \frac{u_K}{u_A} = \frac{2}{1},$$

or, since 3 faradays have passed:

$$v_K = \frac{2}{3} \qquad v_A = \frac{1}{3}.$$

Suppose that the anions which have migrated to K have formed new salt from the electrode material instead of being discharged. In this more usual case, it is required to find the loss of salt due to migration. Without the kathionic migration, the gain of concentration would have been 3; actually the gain is 1; hence $u_K = 2$ and $v_K = \frac{2}{3}$ as above.

Or, in other words, the ratio of actual gain to maximum possible gain of anion is:

$$\frac{u_A}{v_A + u_K} = v_A.$$

Ionic Conductivities l_A, l_K at 18° (Kohlrausch and Holborn).

Gram Equivalents per litre (C).	K.	Na.	Li.	NH_4.	Ag.	$\frac{1}{2}Ba$.	$\frac{1}{2}Sr$.	$\frac{1}{2}Ca$.	$\frac{1}{2}Mg$.	$\frac{1}{2}Zn$.	H.
0·	65·3	44·4	35·5	64·2	55·7	57·3	54·0	53·0	49	47·5	318L_K
0·0001	64·7	43·8	34·9	63·6	55·4	55·0	51·7	50·6	47	45·1	316
0·0002	64·4	43·6	34·7	63·4	55·1	54·3	51·0	50·0	46	44·5	316
0·0005	64·1	43·3	34·4	63·0	54·9	53·3	50·0	48·9	45	43·5	315
0·001	63·7	42·9	34·0	62·7	54·7	52·2	48·9	47·8	43	42·3	314
0·002	63·2	42·4	33·5	62·2	54·2	50·7	47·4	46·4	42	40·9	313
0·005	62·3	41·4	32·6	61·2	53·2	48·2	44·9	43·9	40	38·9	311
0·01	61·3	40·5	31·6	60·2	51·9	45·7	42·4	41·4	37	35·9	310
0·02	60·0	39·2	30·3	59·0	50·0	42·7	39·4	38·3	34	32·9	307
0·03	59·2	38·3	29·4	58·1	48·6	40·5	37·2	36·1	32	30·7	305
0·05	57·9	37·0	28·2	56·8	46·6	37·7	34·4	33·4	29	27·9	302
0·1	55·8	35·6	26·1	54·8	43·3	33·8	30·5	29·4	25	24·0	296

	Cl.	I.	NO_3.	ClO_3.	$C_2H_3O_2$.	$\frac{1}{2}SO_4$.	$\frac{1}{2}C_2O_4$.	$\frac{1}{2}CO_3$.	OH.
0·	65·9	66·7	60·8	56·2	33·7	69·7	63	—	174L_A
0·0001	65·3	66·1	60·2	55·5	33·1	67·2	61	—	172
0·0002	65·1	65·9	60·0	55·2	33·0	66·6	60	—	172
0·0005	64·8	65·5	59·6	54·6	32·8	65·4	59	—	171
0·001	64·4	65·1	59·3	54·1	32·6	64·0	58	69	171
0·002	63·9	64·6	58·8	53·4	32·4	62·3	56	66	170
0·005	63·0	63·7	57·8	52·4	31·6	59·2	54	60	168
0·01	62·0	62·7	56·8	51·3	30·8	56·1	51	55	167
0·02	60·7	61·5	55·6	49·7	29·8	52·3	48	50	165
0·03	59·8	60·6	54·7	48·4	29·0	49·7	46	47	163
0·05	58·6	59·3	53·4	46·4	28·0	46·1	43	43	161
0·1	56·5	57·3	51·4	43·2	26·4	41·9	39	38	157

Reactions in Solution (Heterogeneous).

Distribution Ratio.

If a substance A is distributed between two phases, there is often a constant ratio between the first or some other power of the concentrations in the two phases (C_1, C_2, etc.).

Thus, if the substance in question is hydrogen as gas and dissolved in water

$$H_2 \text{ (gas)} \rightleftarrows H_2 \text{ (dissolved)}.$$

And the concentrations in the gas and solution phases are C_1 and C_2

$$C_1 = KC_2,$$

K being the partition ratio or distribution coefficient of hydrogen between the two phases.

If the substance, *e.g.*, hydrogen, has a different molecular complexity (n_1 and n_2) in the two phases, then, by the laws of chemical equivalence :

$$n_2H_{n_1} \rightleftarrows n_1H_{n_2},$$

e.g. $1\ H_2 \rightleftarrows 2\ H_1$ (for the equilibrium between H_2 as gas and dissolved in certain metals).

$$C_1^{n_2} = KC_2^{n_1}, \quad . \quad . \quad . \quad . \qquad (21)$$

e.g. $C_1 = KC_2^2$ (in the case mentioned above).

Thus, if a series of concentrations C_1 and C_2 corresponding to one another is known, then the ratio between the coefficients n_2 and n_1 of the chemical equation may be determined by finding a power of C which makes the ratio $\frac{C^r}{C_2}$ continually a constant.

The choice of values for r is limited by the laws of chemical combination and by previous knowledge. The index r is obviously equal to $\frac{n_2}{n_1}$, since

$$n_1 \sqrt{K} = \text{constant} = \frac{C^{\frac{n_2}{n_1}}}{C}.$$

The concentrations C_2 and C_1 of the dissolved substance in phases (1) and (2) are for convenience expressed in different units. Thus the relation between the pressure of a gas and the amount dissolved in a liquid is usually expressed as the "absorption coefficient" (Winkler), the "absorption" being the volume of gas (reduced to N. T. P.) which is dissolved by one volume of the liquid.

What is the relation between the unit of "absorption" per litre of the liquid and the unit, 1 gram molecule per litre?

Answer The latter unit is 22·4 times the former.

In the case of many slightly soluble gases (O_2, N_2, etc.), the constancy of the ratio of the pressures (or partial pressures) to the amounts dissolved in solvents, such as water and alcohol (Henry's Law) indicates that the molecular complexity of the gases is the same in the dissolved as in the free state.

On the other hand, a high solubility at atmospheric pressure usually indicates the formation of new kinds of molecules, complexes, etc., from the simplest dissolved molecules. Examples of such solutions are: HCl in water (ions), NH_3 in water (NH_4OH), NH_3 in water + $AgCl$ (complex), SiF_4 in water (H_2SiF_6).

Solubility Product.

As in the case of homogeneous solution equilibria, the examples of heterogeneous equilibria most successfully studied have been those in which the reacting molecules were electrolytes. The relations here met with are well represented by the following conception.

As in the case of isothermal gas equilibria, those molecular species which are present as pure solids and liquids have a constant partial pressure in the reacting mixture, so, in the case of solution equilibria, if a pure solid is present the concentration of its molecules remains constant in the solution kept at the same temperature.*

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* NOTE.—The constancy of the solubility product can be deduced independently of this assumption.

Applying the equilibrium formula to the concentrations of the dissociated and undissociated solute :

$$[a]^m \times [b]^n = K\,[a_m b_n].$$

This result, like other simple deductions from the law of mass action, is best confirmed in the case of dilute solutions. (See J. Walker, Brit. Association Reports, 1911.)

It is known from other evidence that the nature of the solvent is altered by the addition of other solutes, or by the presence of a moderate concentration of the molecule in question. Such alteration is quite sufficient to account for a cessation of the constancy of the solubility product $[a]^m \times [b]^n$ which has been observed in some cases.

PROBLEMS.

Equilibrium in Electrolytes.

✓ **1.** The cell constant Γ is defined as the resistance of the cell when filled with an electrolyte of unit specific conductivity $\Gamma = \kappa R = \frac{l(cm)}{a(cm)^2}$ Such an electrolyte, placed in a U-tube of uniform cross-section (0·5 (cm.)^2) has a resistance of 20 ohms.

What is the distance between the electrodes?

$$R = \frac{l\kappa}{a} \quad l = \mathbf{10}. \quad \text{Answer.}$$

✓ **2.** A solution of $MgSO_4$ has a maximum conductivity of 0·05 at 18°63. It is used to standardise the above cell.

What will be the total resistance at 18°63 ?

Answer $R =$ **400** ohms.

K/R

3. The same solution, put into a vessel of unknown constant was balanced by 100 ohms, in the other arm of the bridge.

What is the cell constant?

Answer **5.**

4. Given two cells of which the constants are known to be of the order of 1,000 and 0·1 (*e.g.*, by measurement), it is required to find the limits between which κ of standardising electrolytes must lie, in order that the balancing resistances in the other arms of the bridge may be between 100 and 1,000 ohms. κ must be not greater than $\frac{1000}{100}$ in the first case, or less than $\frac{1000}{1000}$.

Answer $\kappa = \mathbf{1} \longrightarrow \mathbf{10}$ **and** $\mathbf{0{\cdot}001} \longrightarrow \mathbf{0{\cdot}0001}$.

5. A cell filled with $0{\cdot}001/N{\cdot}KCl$ at 18° ($\kappa = 0{\cdot}001225$) had a resistance of 408 ohms. The same cell filled with water balanced against 50,000 ohms gave a bridge reading of 71·43 corresponding to the cell (28·57 to R in box).

What is κ of the water?

First find the cell constant.

$$R \text{ of cell filled with water} = \frac{a}{b} \times R_{\text{box}} = \frac{71{\cdot}4}{28{\cdot}6} \times 50{,}000$$

Answer $\kappa = \mathbf{4 \times 10^{-6}}$.

6. If the mobilities L^{+} and L^{-} of $H^{\cdot}$ and OH' ions are 312 and 174 at 18°, and the conductivity of pure water (Kohlrausch and Heydweiller) is $0{\cdot}04 \times 10^{-6}$ mhos at 18° how many gram-molecules of dissociated water are there in a litre?

Answer $\mathbf{0{\cdot}8 \times 10^{-7}}$.

$$\eta = \frac{\kappa}{L_A + L_K}$$

7. The equivalent conductivity Λ_0 or Λ is made up additively of the electrolytic mobilities of the ions, either real (L_A, L_K) at complete dissociation, or effective ($a\,L_A$, $a\,L_K$).

Find the value of Λ_0 for $NaNO_3$ from the following:

Salt:	KCl	$NaCl$	KNo_3
Λ_0	129·1	108·1	125·5

Answer **104·5**

8. If the apparent ionic mobilities l_{Na} and l_{Cl} in a normal solution of $NaCl$ are 27·0 and 47·3, find the apparent velocities $\alpha\ U_K$ and $\alpha\ U_A$, and the real velocities U_A and U_K for these ions (Λ_0 for $NaCl = 109{\cdot}7$) $\alpha = \frac{\Lambda}{\Lambda_0}$

Answer:

$U_{Na} = \mathbf{0{\cdot}000494}$ $U_{Cl} = \mathbf{0{\cdot}000523}$ centimetres per second.
$U_{Na} = \mathbf{0{\cdot}00073}$ $U_{Cl} = \mathbf{0{\cdot}000775}$ " " "

9. The velocity of the hydrogen ion has been directly determined by Lodge (Brit. Association Reports (1886), p. 389) to be 0·003 centimetres per second, under unit potential gradient.

What weight (in kilograms) would be required to drive 1 gram ion of hydrogen through acidulated water, at 1 centimetre per second?

Answer **330** million kilograms.

Electric power = 96,540 volt coulombs = $9{\cdot}65 \times 10^{11}$ dynes.

Electric power required for velocity $= \frac{9{\cdot}65 \times 10^{11}}{003 \times 981} =$

$$3{\cdot}3 \times 10'' = 3{\cdot}3 \times 10^8 \text{ kgm.}$$

10. The velocity ($\alpha\ U_K$) of the Na ion in normal $NaCl$ is 0·00028 centimetres per second.

Find the force required to drive 1 gram of $Na^{\cdot}$ of this concentration, at the rate of 1 centimetre per second.

Answer $\frac{9{\cdot}654 \times 10^{11}}{23 \times 981000 \times 0{\cdot}00028} = \mathbf{153 \times 10^6}$ kilograms.

11. The transport number of K in KCl was found to be 0·497, and $\Lambda_0 = 130{\cdot}1$.

What is the absolute velocity of $K^{\cdot}$ in centimetres per second, under unit potential gradient?

1 equivalent of the 2 ions carries 130·1 amperes.

1 equivalent of K carries $130{\cdot}1 \times {\cdot}497 = 64{\cdot}67$.

$$\text{Velocity} = \frac{\text{coulombs per second for 1 gram ion}}{\text{charge on gram ion}}$$

Answer **0·00067** centimetres per second.

The value of κ_{18} for $0{\cdot}884/N{\cdot}\ NaCl = 0{\cdot}0672$; what is the value of Λ?

Answer **76.**

12. A solution containing 5 per cent. of KCl (by weight) has a density of 1·0308. The molecular conductivity is 99·9.

What current will be carried by a cube of 1 litre capacity filled with this solution, if the two opposite sides are made electrodes, and the potential fall is 1 volt per centimetre?

$$\text{Conductance} = \frac{100 \times 0{\cdot}691}{10} = \frac{a\kappa}{l} = \mathbf{6{\cdot}91} \text{ amperes. Answer.}$$

13. The molecular conductivity at infinite dilution of a weak electrolyte cannot be directly determined, since Λ does not approach a limit at the greatest possible dilutions. The required Λ_0 may, however, often be obtained indirectly, from the law of independent migration, of the ions, and from the conductivity of the salt of the weak base or acid.

Given: $L(Na) = 44{\cdot}4$; $L(H) = 318$ $\Lambda_0(NaA) = 78{\cdot}1$, and $\Lambda(HA)$ at $C = 0{\cdot}001$, find $\Lambda_0(HA)$ and $a(HA)$, at the above concentration.

Answer **351·7** and **0·117**

$$\Lambda_0 - L_K = L_A$$

14. The temperature coefficient of conductivity is about 0·02 per degree on each unit of κ. The coefficient (a) of increase of conductivity in the formula given below varies with κ, being:

0·0188 when κ is 0·1359, and
0·0179 when κ is 0·2020 (both at 18°).

If κ and κ_t are the conductivities at 18°, and a temperature not far removed from 18°,

$$\frac{\kappa}{\kappa_t} = \frac{1}{1 + a\,(t - 18)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similarly, of course, for any temperatures t_1 and t_2 in the neighbourhood of 18° :

$$\frac{\kappa t_1}{\kappa t_2} = \frac{1 + a\,(t_1 - 18)}{1 + a\,(t_2 - 18)} \quad . \quad . \qquad (2)$$

Thus, for a *KCl* solution κ was found to be 0·1719 at 20°·6. What is the value of κ at 18° and 25° ?

Answer **0·164** at **18°**, **0·1851** at **25°**.

First find κ_{18} approximately from the rough 0·02 coefficient (a); then obtain the more exact value corresponding to the κ_{18} so found, by interpolation of the given values of "*a*." Then apply equation (1) above.

15. Λ at ·01/N solution is about 100 for most common salts ($\eta = 0{\cdot}0_41$).

Hence $\eta = \dfrac{\kappa}{100}$ $\kappa = 0{\cdot}0_21$.

Hence also, if c is the number of milligram equivalents per litre ($\eta \times 10^6$).

$c = 0{\cdot}0_41 \times 10^6 = \kappa \times 10^4 = 10$ in this case, and as the salts are completely dissociated κ varies directly as c.

If κ for a natural water is $0{\cdot}0_3\,2$, and the average molecular weight of the dissolved salt is taken as 75, find the mineral solids in the water, expressed as parts per million (find C in milligram equivalents as above, and change into grams per thousand litres).

Answer **15** parts per million.

Kohlrausch ("Leitvermogen der Elektrolyte.")

16. The concentrations of electrolytes may be expressed as gram equivalents per kilogram of solution (Γ), and the molecular conductivities Λ_M as conductivities divided by gram equivalents per kilogram of solution $\dfrac{\kappa}{\Gamma}$. If this form of expression is employed, the graph of Λ and Γ is nearly linear for concentrated solutions.

In other words $\Lambda_M = a + b\Gamma$, "a" and "b" being characteristic constants for each electrolyte and temperature. The condition of maximum conductivity being $\frac{d\kappa}{d\Gamma} = 0$, show that the concentration at which the maximum occurs is $-\frac{a}{2\,b}$ gram equivalents per kilogram.

Also calculate this concentration in the case of $\frac{1}{2}$ H_2SO_4 from the following experimental data :

Per cent. H_2SO_4	$10^4\ \kappa$ (18°)	Γ	Λ_M
10	3,915	2·039	192·0
15	5,432	3·059	177·6
20	6,527	4·077	160·1
25	7,171	5·096	140·7
30	7,388	6·116	120·7
35	7,243	7·137	101·5
40	6,800	8·155	83·4
45	6,164	9·177	67·2
50	5,405	10·195	50·8

Answer $a = \mathbf{235{\cdot}5}$

$b = -\mathbf{18{\cdot}7}$

Concentration = **6·298** equivalents per kilogram.

$\kappa_{\text{max.}}$ (18°) = **0·7414**.

J. Gibson (Trans. Roy. Soc. Edin. (1905—1907), 45, 241).

17. The following are the values of Λ at various dilutions for CH_3COOH and NH_4OH ($\Lambda_0 = 388$ and 253). Find the corresponding values of a and K.

	Λ	Λ
CH_3COOH	16	6·5
	128	18·1
	1,024	49·0
NH_4OH	8	3·4
	22	6·7
	128	13·5

Answer for CH_3COOH, $100a = \mathbf{1{\cdot}67, 4{\cdot}68, 12{\cdot}66}$.

,, NH_4OH, $100a = \mathbf{1{\cdot}36, 2{\cdot}65, 5{\cdot}33}$.

$K \times 10^{-5} = \mathbf{1{\cdot}78}$ (CH_3COOH).

$= \mathbf{2{\cdot}3}$ (NH_4OH).

If K for $CH_3COOH = 1{\cdot}78 \times 10^{-5}$,

and, K for $CH_2ClCOOH = 1{\cdot}58 \times 10^{-3}$,

find the degree of dissociation of the former acid at a dilution (V) of 0·994, 18·1, 3,010 and 15,000; and for the latter at $V =$ 20·0, 2,060, and 10,100.

The values $100a$, found by means of Λ and Λ_0 are: **0·40, 1·78, 20·5, 40·8,** and **16·6, 80·6, 94·8** respectively.

Note.—In the quadratic root,

$$a = \frac{-K + \sqrt{K^2 + 4KC}}{2C}$$

where K is small K^2 and K may be neglected in comparison to $\sqrt{K}$, and

$$a = \sqrt{\frac{K}{C}}$$

18. The molecular conductively of H_2CO_3 is 1·033 at a dilution of 27·5 litres to the molecule. The ionic mobility of HCO'_3 is 40·5, that of $H^{\cdot} = 316$; find the degree of dissociation, and the first dissociation constant of H_2CO_3.

Answer $a = \mathbf{0{\cdot}00289}$

$K = \mathbf{3{\cdot}04 \times 10^{-7}}$

$$\frac{1{\cdot}033}{356{\cdot}9} = a$$

$$\frac{a^2}{(1-a)V} = \frac{(2{\cdot}89)^2 \times 10^{-6}}{27{\cdot}5}.$$

Walker and Cormack (*Journ. Chem. Soc.* (1900), 77, 5).

19. The degree of dissociation of the strongest monobasic acids and monacid bases at 0·1/N. concentration is about 0·92.

What is the average dissociation constant?

Answer $K = \mathbf{1{\cdot}05}$.

20. Deduce a general formula for the relation between K, V and a.

The degree of dissociation (at $C = 0{\cdot}0429$ grams in 200 c.c. of water) of C_6H_5COOH is 0·5843.

Find the degree of dissociation of a solution containing 0·2817 grams of the acid in 300 c.c. of water.

Answer $a =$ **0·071.**

Find V in gram molecules per litre, then find K from the first data.

$$a = \frac{KV}{2}\left(\sqrt{1 + \frac{4}{VK}} - 1\right)$$

21. In the case of 1 gram molecule of a salt dissociating into n ions, the apparent number of molecules from one formula molecule, as judged by the lowering of the freezing point, increase of osmotic pressure, etc., is $1 + (n - 1)a = i$ instead of 1. Hence, i may be found from the conductivity measurements,

since $$a = \frac{\Lambda}{\Lambda_0} \text{ and } a = \frac{i - 1}{n - 1}$$

Thus, the value of i for KCl at $C = 0{\cdot}14$ is 1·81, a, therefore $= 0{\cdot}81$. At 18° $\Lambda = 110$, and $\Lambda_0 = 129{\cdot}5$.

$\therefore\ a =$ **0·85** and $i =$ **1·85.**

22. For $CaCl_2$ ($C = 0{\cdot}184$ gram equivalents per litre) i is 2·42. $\Lambda_0 = 115{\cdot}2$.

What is the value of Λ and $10^4\ \kappa$ at this concentration?

Answer $a =$ **81·9.**
$\kappa \times 10^4 =$ **160·6.**

23. The degree of dissociation of $K_4Fe(CN)_6$ at a certain concentration is 0·52. Find i for this dilution, on the assumption that the compound gives the ions $4\ K$ and $Fe(CN)_6''''$.

Answer $i =$ **3·07.**

The value found by the osmotic method was 3·09.

24. What concentration of acetic acid will give a hydrogen ion concentration of 1×10^{-3}?

$$K = 1{\cdot}8 \times 10^{-5}$$
$$[H^{\cdot}]^2 = K[HA]$$

Answer $[HA] = \mathbf{0{\cdot}0577}\ N$ (since the total $[HA]$ is very nearly equal to the undissociated $[HA]$).

Noyes (*Journ. Amer. Chem. Soc.* (1910), 32, 7).

25. From the solubility of CO_2 in water (Problem 69, p. 213), combined with the preceding data (p. 188), find the hydrogen ion concentration of water at 16°, due to CO_2 dissolved from air, assuming all dissolved CO_2 to be present as H_2CO_3.

Answer $[H] = \mathbf{1{\cdot}99 \times 10^{-6}}$.

$$[H] \times [HCO_3] = [H]^2 = K[H_2CO_3] = KK_1P_{CO_2}.$$

What is the conductivity of this solution?

Answer $\mathbf{7{\cdot}13 \times 10^{-7}}$.

$$\kappa = \Lambda_0\eta.$$

26. The dissociation constant of NaH_2PO_4 is $2{\cdot}0 \times 10^{-7}$ at a molecular normal concentration of 0·1, and the degree of primary dissociation into $Na^{\cdot}$ and $H_2PO'_4$ is 0·77 (Abbott and Bray (*Journ. Amer. Chem. Soc.* (1909), 31, 760). What is the hydrogen ion concentration of such a solution?

Here, again, as in the preceding problems in the equation $\dfrac{(aC)^2}{(1-a)C}$, the concentration of undissociated $H_2PO_4(1-a)C$ may be put equal to C, the total phosphoric ion concentration.

Answer $[H^{\cdot}] = \mathbf{1{\cdot}24 \times 10^{-4}}$.

27. By colorimetric tests, a solution of an indicator is prepared, which is exactly half-way between its full acid and alkaline colours. This corresponds to an apparent 50 per cent. dissociation of the indicator acid. Find its apparent dissociation constant from the E. M. F. of the following combinations, the indicator half of the cell being in the condition mentioned.

$$H_2Pt \mid 0{\cdot}01HCl \mid \text{indicator} + \text{acid} \mid H_2Pt.$$

For methyl orange $E = 0{\cdot}077$ volts.
For phenolphthalein $E = 0{\cdot}410$ volts.

Answer $K = 4{\cdot}65 \times 10^{-4}$ and $8{\cdot}1 \times 10^{-10}$.
(See Electromotive Force, p. 252.)

$$E = 0{\cdot}058 \log \frac{0{\cdot}01}{[H]}$$

$$K = \frac{aC[H^{\cdot}]}{(1-a)C}$$

Salm. (*Zeitsch. physikal Chem.* (1907), 57, 492).
Salessky (*Zeitsch. Electrochem.* (1904), 10, 204).

28. The conductivity of absolutely pure water has been deduced from that of the purest that can be prepared, by subtraction of the conductivity due to unavoidable traces of dissolved matter. (Kohlrausch and Heydweiller, *Zeitsch. physikal Chem.* (1894), 14, 326.)

The value finally arrived at was $0{\cdot}0361 \times 10^{-10}$ at 18°, referred to mercury at 18°. The electrolytic mobilities L_A and L_K of $H^{\cdot}$ and OH', expressed in the same units are 290×10^{-4} and 165×10^{-4}. How many gram molecules of dissociated water are there in a litre at 18°?

Defining the ohm as on p. 12, how many of the above mercury units are there in an ohm, if the electrical resistance r of mercury increases above 0° C., according to the equation:

$$r_t = r_0(1 + 0{\cdot}0_39t)\,?$$

Also state the value of L_A and L_K for OH and H in reciprocal ohms, and compare the conductivity of pure water with that of distilled water in contact with the air (Problem 25 above.)

Answer **0·8** $\times$ **10** $^{-7}$ of $H^{\cdot}$ and of OH' (gram ions).
1·08 $\times$ **10** $^{-4}$ mercury units (1 c.c. at 18°) in 1 ohm.

$$L(H^{\cdot}) = 314{\cdot}0.$$
$$L(OH') = 1{\cdot}785.$$

The water containing CO_2 absorbed from the air has a conductivity approximately **20 times** that of pure water.

Note.—See Table, p. 179, for the accepted values of the ionic conductivities of $H^{\cdot}$ and OH'.

29. How much Na acetate + 3 H_2O will have to be added to 0·1 N. acetic acid (1 litre) in order that the hydrogen ion concentration may be 1×10^{-4} (assume the NaA to be completely dissociated).

$$NaA = 0{\cdot}02 \text{ mols. per litre.}$$

Answer **2·7 grams** of crystalline salt.

The concentration of the acetyl ion to be added A' is first calculated from the approximate equation, $[A'] \times [H^{\cdot}] = K[HA]$.

The degree of dissociation at the found concentrations is not 1, but 0·9. Substitute this again to get the more exact value of $[NaA]$.

30. A 0·1 N. solution of Na_2HPO_4 is assumed to be completely dissociated with respect to Na. The addition of dilute HCl (also assumed completely dissociated), converts HPO''_4 quantitively into H_2PO_4', which ionises, the constant being 2×10^{-7}. Find what quantities of the 0·1 solutions of the phosphate and HCl must be mixed, in order that the hydrogen ion concentration may be 1×10^{-7} (neutral point, pure water).

$$\frac{[H_2PO'_4]}{[HPO''_4]} = \frac{[H^{\cdot}]}{2{\cdot}0 \times 10^{-7}}$$

Answer **1** volume of HCl.
2 volumes of Na_2HPO_4.

31. Two salts (1) and (2), separately dissolved in water to a given concentration (say 1 per cent. by weight) are each fully ionised. A solution containing 1 per cent. by weight of a mixture of the two is also fully ionised.

The conductivities of the separate salts are κ_1 and κ_2, and that of the mixture containing x_1 per cent. of (1) and $1 - x_1$ per cent. of (2) is κ.

Then $\kappa = x_1\kappa_1 + (1 - x_1)\,\kappa_2$ or $x_1 = \dfrac{\kappa_2 - \kappa}{\kappa_2 - \kappa_1}$.

A mixture of KI and KCl made up to a certain concentration in water had a conductivity of 0·9845. The conductivities of the pure salts at the same total concentrations were 0·8900 and 1·8653 respectively. Find the percentage of KCl in the mixture.

Answer **9·69** per cent. of KCl.

32. If there is a mixture of two electrolytes of concentration C_1 and C_2, with a common ion and equal dissociation constants K_1 and K_2; show that the degree of dissociation must be the same for each, and equal to that which would prevail if each were separately present in the concentration $(C_1 + C_2)$ (Arrhenius).

$$K_1 = K_2 = K = \frac{(a_1C_1 + a_2C_2)a_1C_1}{(1 - a_1)C_1} = \frac{(a_1C_1 + a_2C_2)a_2C_2}{(1 - a_2)C_2}$$

$$\frac{a_1}{1 - a_1} = \frac{a_2}{1 - a_2} = \frac{K}{a_1C_1 + a_2C_2}$$

$\therefore a_1 = a_2 = a$

and $$\frac{a^2(C_1 + C_2)}{1 - a} = K.$$

33. It has been found that when violuric acid 0·01562 N. was mixed with paraoxybenzoic acid 0·01064 N. the degree of dissociation of the former, as judged by its colour, was 3·11 per cent.

Given that $K_1 = 0{\cdot}0_4272$ and $K_2 = 0{\cdot}0_4286$, find the concentration of each anion, (1) violuric, (2) paraoxybenzoic.

Answer (1) **0·0501.**
(2) **$0·0_3342$.**

First verify the found value of a (3·21 per cent.) from the preceding calculation. Take the common dissociation constant as the mean of those for the two acids.

Donnan (*Zeitsch. physikal Chem.* (1896), 19, 480).

34. It is required to mix $CH_2OH \cdot COOH$ ($K_2 = 15 \times 10^{-5}$) with 0·1 N. $CH_3\ COOH$ ($K_1 = 1·8 \times 10^{-5}$), in such a manner that there is no change in the hydrogen ion concentration. What concentration of glycollic acid is required ?

$$\frac{C_2}{0·1} = \frac{1·8 \times 10^{-5}}{15 \times 10^{-5}}$$

Answer $C_2 =$ **0·0172** N.

Show that the conductivity of such a mixture is

$$\frac{\kappa_1 V_1 + \kappa_2 V_2}{V_1 + V_2}$$

(See Introduction, p. 174.)

35. A 0·001 N. solution of sodium acetate has $\Lambda = 75·2$ at 18°, $L_{Na} = 44·4$; $L_{A'} = 33·7$.

What concentration of acetic acid can be mixed with this without change of a?

Answer **0·051** N.

$$a_{NaA} = 0·962,\ [A] = 0·00096 = aC.$$

For the acetic acid $[aC]^2 = K(1 - a)C$, $1 - a = 1$ nearly; $C = 0·051$, and a is small compared to 1, therefore the second approximation is not necessary.

36. From the equation (12), p. 175, calculate the ratio in which the dissociations β_1 and β_2 of $CH_3\ COOH$ ($K_1 = 1·8 \times 10^{-5}$) and $CH_2 \cdot CN \cdot COOH$ ($K_2 = 370 \times 10^{-5}$) are thrown back from the original values a_1 and a_2, when to 1 litre of normal acetic acid is added 1 gram molecule of cyanacetic acid, and *vice versa.*

$$\frac{\beta_1}{\alpha_1} = \sqrt{1 + 205 \times 1}, \text{ etc.}$$

Answer. The ratios of the degrees of dissociation before and after mixing are :

for acetic acid **14·4**;
for cyanacetic acid **1·0049.**

37. It is required to make 1 litre of a mixture containing 0·1 mol. each of acetic and glycollic acids, without altering their degrees of dissociation. What volumes and concentrations of each acid would be taken?

Let C_1 and C_2 be the concentrations ($CH_3\ COOH$ and $CH_2\ OH{\cdot}COOH$), and V_1 and V_2 the volumes.

The following conditions must be satisfied :

$$(1)\ \frac{C_1}{C_2} = 8{\cdot}3;\ (2)\ C_1V_1 = C_2V_2 = 0{\cdot}1;\ (3)\ V_1 + V_2 = 1{\cdot}0.$$

Answer $V_1 =$ **107·5** cubic centimetres.
$V_2 =$ **892·5** „ „
$C_1 =$ **0·93** „ „
$C_2 =$ **0·112** „ „

38. Acetic acid (0·02 $N.$) is mixed with an equal volume of cyanacetic acid (0·02 $N.$). If the separate conductivities at 0·01 normality are 0·143 and 1·57, what is the joint conductivity of the mixture?

For the relation between the degrees of dissociation of the 0·01 $N.$ acids alone, and in the presence of one another, see Problem 36.

$$\frac{\Lambda\ (HA \text{ in mixture})}{\Lambda\ (HA \text{ pure})} = \frac{\alpha_1}{\beta_1}$$

and so for the other acid.

$$\Lambda\ (\text{total mixture}) = \Lambda\ (HA) + \Lambda\ (HA_1)$$
$$\kappa\ (\text{mixture}) = \Lambda\ (\text{mixture}) \times \text{total concentration.}$$

Answer κ mixture = **3·144.**

Note that this is nearly the same as the conductivity of the stronger acid at that concentration.

39. The conductivity of a solution of cyanacetic acid isohydric with 0·01 *N.* acetic is 0·46.

What is the joint conductivity of the two acids in 0·1 normal concentration?

Answer **0·3015.**

40. Let a solution contain equivalent quantities of an acid and two bases (or a base and two acids). The dissociation constants of the bases (acids) being K_1 and K_2, let the share of the bases (acids) appropriated by each acid (base) be x and $1 - x$ respectively. Then it can be shown that:

$$\frac{x}{1-x} = \sqrt{\frac{K_1}{K_2}}.$$

The dissociation constant of NH_4OH is $2{\cdot}3 \times 10^{-5}$, that of $NH_2(CH_3)OH$ is $51{\cdot}98 \times 10^{-5}$.

Find the number of equivalents of HCl appropriated by each in 1 litre of a solution *N.* 8 in respect of each base and the acid.

Answer **0·104** equivalents combined with methylamine.
0·021 equivalents combined with ammonia.

41. A salt of weak base and strong acid is 61·8 per cent. hydrolysed at $C = 0{\cdot}1$ mol. per litre, and 91·6 per cent. at $C = 0{\cdot}001$ mol. per litre.

$$K_w = 1 \times 10^{-14}.$$

What is the hydrolysis constant?

$$K_h = \frac{({\cdot}916)^2 \times 0{\cdot}001}{0{\cdot}084}$$

Answer **1 × 10⁻²**.

42. The degree of hydrolysis of normal NH_4Cl is known to be negligible compared to 1. If K, for NH_4OH is $2{\cdot}3 \times 10^{-5}$ at 25° and K_w is 1×10^{-14}, what is the hydrogen ion concentration in a normal solution of NH_4Cl? Its dissociation can be neglected, and we put $\beta c = [H^{\cdot}] = [NH_4OH]$ as before.

Answer $[H^{\cdot}] = \mathbf{2 \times 10^{-5}}$.

Walker found that $K(HCN) = 1{\cdot}3 \times 10^{-9}$.

$$K_w = 1 \times 10^{-14}$$

Hence calculate the hydrolysis constant K_h of KCN.

Answer **$0{\cdot}9 \times 10^{-5}$.**

43. Shields, by another method, found the percentage hydrolysis of KCN to be: 0·31 at $C = 0{\cdot}947$, and 2·34 at $C = 0{\cdot}024$. Find the corresponding values of K_h.

Answer **0·9 or $1{\cdot}3 \times 10^{-5}$.**

44. Taking K_h as $1{\cdot}1 \times 10^{-5}$, the degree of hydrolysis at any concentration may be found from the approximate formula:

$$x = \sqrt{\frac{K_h}{C}}$$

Hence, find the concentration of OH' ions in a 0·2 N. solution of KCN.

Answer **$1{\cdot}5 \times 10^{-3}$.**

Shields (*Zeitsch. physikal Chem.* (1893), 12, 167).

45. A normal solution of HCl, mixed with varying quantities of urea, inverted solutions of cane sugar, with varying velocities. If the rate of inversion is proportional to the hydrogen ion concentration, and the HCl not united to the urea is assumed fully dissociated, calculate the relative rates of inversion of the original acid, and of the acid after the addition of 2 N urea; if $K_h = 0{\cdot}77$ $0{\cdot}77 = \frac{[H^{\cdot}] \times [BOH]}{[\text{salt}]}$ $[H^{\cdot}] + [\text{salt}] = 1$, $[BOH] + [\text{salt}] = 2{\cdot}0$.

Answer $[H^{\cdot}] =$ **0·36** and the rate of inversion = **0·36** of the former value.

Walker (*Zeitsch. physikal Chem.* (1889), 4, 319).

46. Assuming that Na acetate and $NaOH$ formed by hydrolysis are completely dissociated, but that the acetic acid formed is not dissociated, compare the concentration of

$H^{\cdot}$ and OH' in a 0·1 N. solution of Na acetate, with the ionic concentration of pure water.

$$K_w = 1{\cdot}2 \times 10^{-14}. \quad K_A = 1{\cdot}8 \times 10^{-5}.$$

Answer $h = [OH] = \mathbf{0{\cdot}8 \times 10^{-5}}$
$[OH]$ in water $= \mathbf{1{\cdot}1 \times 10^{-7}}$

47. If K_B and K_A are dissociation constants and $\beta =$ the degree of hydrolysis, etc.

then $$K_B = \frac{[B^{\cdot}] \times [OH']}{BOH}; \; K_A = \frac{[A'] \times [H^{\cdot}]}{HA}$$

(See equations (14), etc., p. 176.)

Undissociated base = undissociated acid = βc (BA being supposed fully dissociated).

Find the degree of hydrolysis h for aniline acetate, from the following:

h, as found by the independent measurements of Arrhenius and Walker is 0·557. $K_w = 1{\cdot}2 \times 10^{-14}$. At a dilution of 256 litres to 1 mol., Bredig found that $h = 8 \times 10^{-2}$ for aniline hydrochloride. K_A, for acetic acid, as before $= 1{\cdot}8 \times 10^{-5}$.

Answer The percentage hydrolysis = **54·4.**

First determine K_B, then the degree of hydrolysis of the weak acid and base.

Abegg ("Ahrens Sammlung," 8).

48. A solution containing 0·0238 mols. of Na_2CO_3 to the litre was found by the method of saponification to be 0·00338 normal, with respect to $[OH]$. By analogy with Na_2SO_4, it is estimated that Na_2CO_3 at this concentration is primarily dissociated ($Na^{\cdot}$ and CO''_3), to 74 per cent.

Find the second dissociation constant of H_2CO_3, the value of K_w at the temperature in question (24°·2) being $1{\cdot}04 \times 10^{-14}$.

Answer $K_2 = \mathbf{1{\cdot}3 \times 10^{-11}}$

$$CO''_3 + HOH = OH' + HCO'_3$$

$$K_2 = \frac{H^{\cdot} \times CO''_3}{HCO_3} \quad . \quad H^{\cdot} = \frac{K_W}{OH'}.$$

Shields (*Zeitsch. physikal Chem.* (1893), 12, 175).

Bodländer (*loc. cit.*, Problem 85, p. 221).

49. How much free acid and ammonia are there in 1 litre a $0{\cdot}1/N$ solution of ammonium acetate at 40° (see Problem 17, p. 188)?

$$K_w = 3 \times 10^{-14}.$$

(Use equation (16), p. 177.)

Answer **0·00085** mols. of each.

50. The first hydrogen ion of H_3PO_4 is that of a strong acid; the dissociation constant of the second $H^{\cdot}$ is $2{\cdot}0 \times 10^{-7}$, and that of the third $H^{\cdot}$ is of the order of 1×10^{-12}.

A mixed solution of $NaOH$ and H_3PO_4 contains the molecules: NaH_2PO_4, H_3PO_4, Na_2HPO_4, Na_3PO_4, and $NaOH$; and the ions: $Na^{\cdot}$, $H_2PO'_4$, HPO''_4, PO'''_4, and OH'.

If the stoichiometrical proportions of $NaOH$ and H_3PO_4 lie between NaH_2PO_4 and $NaH_2PO_4 + 0{\cdot}75\ NaOH$ ($[H^{\cdot}]$ between 1×10^{-4} and 5×10^{-8}), the concentrations of H_3PO_4, Na_3PO_4 and PO'''_4 are vanishingly small compared with those of the other molecules, and the constant K_3 does not come into consideration. If, in addition the total salt concentration is large compared to $[H^{\cdot}]$ or $[OH']$, the alkalinity (acidity) of the solutions is controlled by the ionic and molecular concentration mentioned above, and by the dissociation constant.

Thus, if x_1 = total mols. of phosphoric acid present as HPO_4 (*i.e.*, undissociated Na_2PO_4 or HPO'_4 ion.),

x_2 = total mols. present as H_2PO_4 (dissociated and undissociated).

And if a_1 and a_2 are the degrees of dissociation of Na_2HPO_4 and NaH_2PO_4,

Show that:

$$H_3PO_4 \text{ (total in 1 litre)} = \frac{HPO'_4}{a_1} + \frac{H^{\cdot} \times HPO'_4}{a_2K_2}$$

$$= x_1 + \frac{a_1H^{\cdot}x_1}{a_2K_2}$$

$$\text{and } NaOH = 2x_1 + \frac{a_1H^{\cdot}x_1}{a_2K_2}$$

(total in 1 litre).

The following refer to solutions decinormal with respect to total $H_3PO_4(x_1 = 0{\cdot}1)$

$$K_2 = 2{\cdot}0 \times 10^{-7}$$
$$a_1 = 0{\cdot}6, \ a_2 = 0{\cdot}77.$$

Putting in these numerical values, find the hydrogen ion concentration of a solution containing 196·3 c.c. of normal $NaOH$, and 100·0 c.c of H_3PO_4, made up to 1 litre.

Also in what ratio must $NaOH$ and H_3PO_4 be mixed, in order that the solution may be neutral at 16° (*i.e.* $[H^{\cdot}] = 0{\cdot}73 \times 10^{-7}$)?

Answer (1) $[H^{\cdot}] = 1 \times 10^{-8}$;
(2) **17·7** c.c. of $NaOH$;
and **10·0** of H_3PO_4 made up to 100 c.c.

Abbott and Bray (*Journ. Amer. Chem. Soc.* (1909), 31).
Prideaux (*Journ. Chem. Soc.* (1911), 99, 1224).

Migration Ratio and Ionic Velocities.

51. A solution of $NaCl$ containing 0·2081 gram of $NaCl$ in 100 grams of solution was electrolysed with a Zn anode, using a current which deposited 0·4125 gram of silver in a coulombmeter in series.

The anode solution was now found to contain 0·1375 gram of Cl in 100 grams of solution. If the total weights of the anode solution before and after electrolysis are 718·1 and 719 grams, what is the transport number of Cl?

Answer **0·603.**

Calculate the grams of Cl' required to transport the number of coulombs; then the increase of Cl' in the whole anode solution.

Foerster ("Elektrochemie Wässriger Losungen").

52. A 2 $N.$ solution of HCl (3 litres) is divided by diaphragms into three equal parts: Anode (A), central, and kathode (K).

A current of 5 amperes is passed for ten hours between unattackable electrodes.

The transport numbers of $H^{\cdot}$ and Cl' being $\frac{5}{6}$ and $\frac{1}{6}$, compare the changes of concentration in A and K with the changes of concentration which would prevail in the cell, if the contents were not separated by diaphragms and were well stirred during electrolysis.

Answer. Without diaphragms C falls to **1·38**; with diaphragms C in $A =$ **0·45.**
C in $K =$ **1·69.**

In practice, of course, much oxygen would be evolved with the chlorine, and a certain amount of the latter would remain dissolved.

53. A migration cell contained a solution of $AgNO_3$. At the beginning 12·31 grams was equivalent to 26·55 c.c. of $\frac{N.}{50}$ $KCNS$.

The anode was silver, the kathode copper in concentrated $Cu(NO_3)_2$ (to avoid gassing).

In series was placed a titration voltameter consisting of $NaNO_3$ solution, with a silver anode and a kathode of platinum in HNO_3.

After two hours, at about 10 milliamperes the $AgNO_3$ formed in the voltameter was equivalent to 36·16 c.c. of the $KCNS$ solution, while the anode solution of the cell weighing 23·38 grams was equivalent to 69·47 c.c. of the $KCNS$ solution.

Find the transport numbers of Ag and NO_3. If the solution did not change much in concentration, it would be possible to calculate directly in terms of $KCNS$.

Show that this approximate calculation gives

$$\frac{u_K}{u_A + u_K} = 0·474.$$

$AgNO_3$ in the anode solution $= \dfrac{26·56 \times 170}{50 \times 1000}$ grams in 12·31.

∴ 1 gram of water contained 0·00739 $AgNO_3$ before the electrolysis.

The anode solution after the electrolysis contained

$$\frac{69·47 \times 170}{50} = 0·361 \text{ gram of } AgNO_3.$$

∴ the weight of the water was 23·14 grams.

23·14 grams of water before electrolysis contained 0·1710 gram of $AgNO_3$.

23·14 grams of water after electrolysis contained 0·2361 gram of $AgNO_3$.

Increase $= 0·0651$ gram of $AgNO_3 = 0·000383$ equivalent.

Total silver dissolved $= 0·03616 \times \dfrac{1}{50} = 0·000723$ equivalent.

$$\frac{\text{Loss due to migration}}{\text{Total ions passing}} = \frac{0·000723 - 0·000383}{0·000723} = 0·470.$$

Answer $v_K = \mathbf{0·47}$.

$v_A = \mathbf{0·53}$.

Ostwald-Luther (" Phys. Chem. Messungen," p. 505).

54. A cell, consisting of a copper kathode in $Cu(NO_3)_2$ and an anode of amalgamated cadmium, in a solution of KCl is used to measure the transport numbers of K and Cl.

Show that the total gain of Cl in the anode compartment = the migration gain of Cl in the anode compartment = the migration loss of Cl in the kathode compartment.

In the voltameter in series with the above cell 0·4176 gram of Ag were deposited.

The anode solution contained, after the electrolysis, 0·5240 gram of Cl in a given weight of water, which had previously contained 0·01281 equivalent.

Find the transport numbers of Cl and K.

Answer $\nu_A =$ **0·504.**
$\nu_K =$ **0·496.**

55. A solution of $CuSO_4$, containing originally 0·02547 equivalent of $CuSO_4$ in 50·11 grams of water, was electrolysed with a copper-plated anode and a platinum kathode.

At the anode, a certain amount of Cu_2O was formed which has been calculated as Cu.

The equivalents of Cu on the anode before, and of $Cu + Cu_2O$ after, were 0·0693 and 0·06467, and the solution contained 0·02869 equivalent (SO''_4) and 0·02857 equivalent ($Cu^{\cdot\cdot}$), after the electrolysis.

Find the transport numbers of Cu and SO_4, the weight of copper deposited on the kathode, and the actual loss of weight of the anode.

Answer $\nu_K =$ **0·33.**
Cu deposited on kathode = **0·1522.**
Loss of weight from anode = **0·0852.**

First calculate the net loss or gain of Cu from the anode compartment $= \nu_K$.

The gain of SO_4 in the anode $= \nu_A$, since the current is carried only by $Cu^{\cdot\cdot}$ and SO''_4.

The difference between Cu and SO_4 in the anode compartment after electrolysis is evidently due to simultaneous formation of H and Cu_2O. The Cu_2O will decrease the apparent loss from the anode in a way that has been allowed for above.

The loss of kation from the anode compartment = 0·06938 − 0·06467 − (0·02857 − 0·02547) equivalent = 0·00161 = u_K.

The gain of SO_4 in the anode = u_K = 0·02869 − 0·02547 = 0·00322 = u_A.

Hence, calculate $\dfrac{u_K}{u_A + u_K} = v_K$.

The grams of Cu deposited on the kathode = $(u_A + u_K)\,32·5$.

56. An electrolyte, such as KCl in water and gelatine (to prevent diffusion), is interposed between the anode and kathode compartment of a cell. These compartments respectively contain solutions of $CuSO_4$ and K_2CrO_4 (or other coloured kations and anions which move more slowly than K and Cl). When a current is passed, the motion of the faster moving ions K and Cl is rendered visible as the motion of coloured boundaries. The reason is that the slower moving ion is driven along by the steep potential gradient set up during electrolysis.

Masson (*Zeitsch. physikal Chem.* (1899), 29, 501).

The ratio of the length of the blue section $(Cu)^{\cdot\cdot}$ to the yellow $(CrO_4)''$ at any time was as follows:

All salts were 0·5 normal.

KCl	$NaCl$	Na_2SO_4	$MgSO_4$
1·021	0·671	0·765	0·463

(1) What is the transport number of the anion in the salts?

(2) Also compare the equivalent conductivities: of $K^{\cdot}$ with $Na^{\cdot}$; of Cl' with SO''_4; and of $Mg^{\cdot\cdot}$ with $Na^{\cdot}$.

Assuming equal dissociation.

Answer (1) $v_A =$ **0·495** (KCl) **0·598** ($NaCl$)
0·567 ($\frac{1}{2}Na_2SO_4$) **0·684** ($\frac{1}{2}MgSO_4$).

$v_A = \dfrac{1}{1 + \dfrac{aU_K}{aU_A}}$ and $\dfrac{aU_K}{aU_A}$ is known from the above.

(2) If there are two ions *a* and *b* of valencies (n) 1 and 2, moving at the same speed, the equivalent conductivities of the two ions are also equal.

$$\frac{l_b}{l_a} = \frac{U_b}{U_a}$$

Answer $\frac{l_K}{l_{Na}} = \frac{u_K}{u_{Na}}$ or $\frac{u_K}{u_{Cl}} \cdot \frac{u_{Cl}}{u_{Na}} = 1{\cdot}52.$

$$\frac{Cl'}{SO''_4} = 1{\cdot}14 \qquad \frac{Mg^{\cdot\cdot}}{Na^{\cdot}} = 0{\cdot}60.$$

57. The velocities of the ions can also be measured directly, by observing the rate of motion of a boundary between a concentrated and dilute solution, without the use of a jelly.

Steele (*Zeitsch. physikal Chem.* (1902), 40, 689).

Denison and Steele (Phil. Trans. (1906), 205A, 449).

The velocities directly observed for $K^{\cdot}$ and Br' under unit potential gradient, in 0·1 N. solution of KBr, were $0{\cdot}0_3656$ and $0{\cdot}0_3710$ centimetre per second at 25°.

Find the molecular conductivity Λ.

The velocities observed are the apparent velocities aU_A and aU_K.

Answer $\Lambda = 131{\cdot}9$.

58. The velocities of $Ba^{\cdot\cdot}$ and Cl' in 0·1 $N.BaCl_2$ were found to be, $0{\cdot}0_3452$ and $0{\cdot}0_3638$ centimetre per second at 25°. Find the transport number of the anion and the specific conductivity.

Answer $v_A = 0{\cdot}584$. $\kappa = 0{\cdot}01012$.

59. The electrolytic alkali process depends upon the formation of OH' at the kathode. The ions carrying the current are, on the one hand, $K^{\cdot}$, and, on the other, OH' and Cl'. The products obtained are, at the kathode, hydrogen, at the anode, oxygen and chlorine.

Since the alkali is the most important product, it is necessary to consider only the kathodic current efficiency.

This is given by the ratio of the number of equivalents of KOH actually formed, to the maximum number of equivalents of KOH corresponding to the current used.

The efficiency depends upon the amount of OH passing through the diaphragm, and therefore, upon the proportion of the total current carried by $KOH(x)$ and $KCl(1-x)$ across the diaphragm, *i.e.*, upon the transport number OH' in $KOH(\kappa_2)$, and the transport number of Cl' in $KCl(\nu_1)$.

Let κ_1 and κ_2 be the conductivities of KCl and KOH, and A_1 the current efficiency defined as above.

$$\frac{1-x}{x} = \frac{\kappa_1}{\kappa_2} = \frac{a_1 C_1 (\Lambda_0)_1}{a_2 C_2 (\Lambda_0)_2}$$

$$x = \frac{1}{1 + \dfrac{a_1 C_1 (\Lambda_0)_1}{a_2 C_2 (\Lambda_0)_2}} \quad . \quad . \quad . \quad . \quad (1).$$

For each equivalent of KOH formed, the kathode chamber loses ν_1 of KCl when there is very little KOH in the solution; on the other hand, when there is excess of KOH the kathode chamber loses ν_2 of KOH. The alkali current efficiencies (A) in the two cases will be 1 and $1-\nu_2$.

When there is x of KOH to $1-x$ of KCl (well mixed) in the kathode chamber the alkali current efficiency A will be equal to $1 - x\nu_2$.

The current yield at any moment $\frac{dx}{dI}$ may thus be calculated from the analytical composition of the kathode chamber (C_1 of KCl and C_2 of KOH).

The integral current yield as defined above may be obtained by dividing the number of equivalents of alkali formed in a given time by the number of equivalents of copper deposited in a coulombmeter in series. (See Foerster, "Elektrochemie Wässriger Losungen.")

The following results have been selected from the work of Foerster u. Jorre (*Zeitsch. anorg. Chem.* (1899), 23, 158).

The electrolyte was a solution of KCl, from which during the first and second two-hour periods 17·78 and 14·29 grams of KOH were produced, the copper deposited by the current during the same two periods being 11·47 and 11·71 grams.

At the end of the first two hours, the equivalents of KCl and KOH present in 100 c.c. of solution were 0·2382 and 0·0418; at the end of the second two hours, 0·2224 and 0·0754 respectively.

Calculate: (1) the mean current yield during the second two-hour period; (2) the current yield per second at the end of the second two-hour period, from the following values of the transport numbers ν and the limiting molecular conductivities Λ_0.

KCl.	*KOH.*		
If $C = 2$	If $C = 0·2$	0·5	1·0
$\nu_1 = 0·515$	$\nu_2 = 0·736$	0·738	0·74
$\Lambda_0 = 129·07$	$\Lambda_0 = 235$		

Answer **69·30** and **70·4** per cent.

60. At the end of the sixth hour the equivalents of KCl and KOH present in 100 c.c. were 0·2096 and 0·1071, at the end of the eighth hour 0·2066 and 0·1331, respectively.

Hence, calculate the mean current yield over the whole eight hours, and compare it with the mean current yield over the four-hour period previously considered.

Answer 71 per cent. and 78 per cent.

Draw the graphs of the current yield $\frac{dx}{dI}$ and of the total alkali x, both against time.

Note.—In this problem a_1 is assumed to be equal to a_2 in equation (1).

Using equation (1) of last problems, compare the current efficiencies in the case of KCl and $NaCl$ at the end of an electrolysis, at which time the kathode liquors are found to be double normal, with respect to chloride, and normal, with respect to alkali.

$$v_A\,(KOH) = 0{\cdot}74 \qquad v_A\,(NaOH) = 0{\cdot}825$$

$$L_K = 65{\cdot}3 \quad L_{Na} = 44{\cdot}4 \quad L_{Cl} = 65{\cdot}9 \quad L_{OH} = 174$$

Answer For KCl **64·8** per cent.
For $NaCl$ **59·2** per cent.

61. It was not found profitable to continue an electrolysis of $NaCl$ after the current efficiency had fallen below 80 per cent.

What is the ratio of chloride to alkali at this point?

If the solution is now double normal with respect to $NaCl$, find the alkali concentration.

$$\text{Answer} \quad \frac{[NaCl]}{[NaOH]} = 6{\cdot}15 \quad [NaOH] = 0{\cdot}325$$

62. The Le Chatelier-Van't Hoff principle of equilibrium displacement may be applied to reactions in solution, if: Q = the heat absorbed on dissociation, and K = the dissociation constant as defined above,

$$\frac{d \log K}{dt} = \frac{Q}{RT^2}$$

The dissociation constant of water at 0° is 0·12, and at 2° is 0·15 (Kohlrausch and Heydweiller). Find the heat evolved on the combination of 1 gram equivalent of $H^{\cdot}$ with 1 of OH', to form liquid water at 1°, assuming that Q can be taken as constant over this range.

Answer Q = **16,700** calories.

Ionic product of water × 10^{14} (Lunden):

	0°	10	18	25	40	50	100	218	306
Löwenherz .				1·41					
Kohlrausch and Heydweiller .	0·12	0·31	0·64	1·11	3·26	6·15	(72)		
Lunden . .	(0·12)	0·31	0·62	1·05	2·94	5·17	(33)		
Noyes . .	0·09		0·46	0·82			48	461	168 ?

( ) = extrapolated.

63. The heat of dissociation of water has been expressed by the interpolation formula:

$$Q = \frac{4{\cdot}045 \times 10^{-6}}{T} \text{ calories.}$$

Hence, if the dissociation constant $K_w = 0{\cdot}12 \times 10^{-14}$ at 0° C., find K_w, at 18° C.

$$\int d \log K = \int \frac{Q}{R} \frac{dt}{T^2} = \int \frac{4{\cdot}045 \times 10^{-6}}{RT} \frac{dT}{T^2} = \frac{-4{\cdot}045 \times 10^{-6}}{2\,RT^2}$$

Answer $K_w = \mathbf{0{\cdot}62 \times 10^{-14}}$ (18°).

64. From the calorimetric measurements of many experimenters, the heat of ionisation of water may be expressed by:

$$Q = -14{,}700 + 50\,t \text{ calories.}$$

The dissociation constant for the first $H^{\cdot}$ of boric acid is 5·8 at 18°, and 8·5 at 40°.

Assuming that the heat of dissociation (Q_d) does not alter much over this range of temperature, calculate Q_d and the heat of neutralisation (Q_n) at 29°.

$$Q_n = Q_d - Q = + \mathbf{10{,}210}.$$

Lunden ("Ahrens Sammlung," 14).

Distribution Ratio.

65. Acetic acid is partly associated into double molecules, both in benzene solution at 80°, and in the vapour in equilibrium with it.

If the total concentrations C_V and C_L, and the degrees of dissociation a_V and a_L, in the vapour and liquid phases are known, then the distribution ratios K_1 and K_2 of the single and double molecules can be calculated.

Nernst (*Zeitsch. physikal Chem.* (1891), 8, 110).
Aulich (,, ,, ,, (1891), 8, 105).

The degree of dissociation of the double molecules in solution a_L was ascertained from the elevation of the boiling point of an acid which is non-volatile, but similar to acetic acid in other respects. The elevation of the boiling point of the acetic acid in benzene is then determined. The difference between this observed elevation and the elevation calculated for the total concentration of the double molecules in liquid (dissociated to the degree a_L as above) gives the partial pressure of the acetic acid in the vapour. (See Dilute Solutions, p. 92.) This combined with the Gibbs formula:

$$\log \frac{2{\cdot}073\,(D - 2{\cdot}073)}{(4{\cdot}146 - D)^2\,P} = \frac{3520}{T} - 11{\cdot}349$$

(which gives the relative density D (air = 1) of the acetic acid vapour at any pressure) leads directly to a_V, the degree of dissociation of the double molecules in the vapour.

The number of single molecules in the vapour is proportional to the pressure p, to the density D (air = 1), and also to the degree of dissociation a_V of the double into single molecules.

At a temperature of 80° C., solutions of 0·663 and of 8·42 grams of acetic acid, in 100 grams of benzene were found to be dissociated to 10 per cent. and 2·9 per cent., respectively, into single molecules.

The total pressures of acetic acid in the vapour from these two solutions were 6·5 and 36·4 mm.

The density of $C_6H_6 = 0{\cdot}815$.

What is the distribution ratio of the single molecules, between the vapour and the liquid?

$$\text{Find } a_V, \text{ from } a_V = \frac{4{\cdot}146 - D}{D},$$

And deduce as above that the number of single molecules in 1 litre of vapour is proportional to:

$$p\,(4{\cdot}146 - D).$$

Also the number of single molecules in 1 litre (solution)

$$= K a_L\, C_L.$$

The distribution ratio for the single molecules $\frac{\text{vapour}}{\text{solution}}$

$= \mathbf{167{\cdot}2}K'$ and $\mathbf{167{\cdot}8}K'$. Answer.

(K' contains all the constants of proportion.)

What is the numerical value of the dissociation isotherm in the solution?

$$K = \frac{[CH_3COOH]^2}{[(CH_3COOH)_2]}$$

Answer $K = 0{\cdot}0292$ for each concentration.

66. The distribution of benzoic acid (C_6H_5COOH) between benzene and water has been investigated by Nernst (*Zeitsch. physikal Chem.* (1891), 8, 110), and by Hendrixson (*Zeitsch. anorg. Chem.* (1897), 73, 13).

The following are the total concentrations (in grams to 200 grams solvent) of the acid, in the two phases, at 10°.

C_W	C_B
0·0429	0·1449
0·1124	0·8843
0·2817	5·4851

The dissociation constant of benzoic acid in water is $0{\cdot}0_46$.

If β is the degree of association of the single (C_6H_5COOH) to the double $(C_6H_5COOH)_2$ molecules in the benzene, and a is the degree of dissociation of the C_6H_5COOH molcules to the ions ($H^{\cdot}$ and C_6H_5COO') in the water;

then $\therefore K_B = \dfrac{C_B(1-\beta)^2}{\beta}$ (association constant) . (1)

$K_W = \dfrac{C_W\,a^2}{1-a}$ (dissociation constant) . . (2)

The only molecules common to the two solvents are the single (C_6H_5COOH).

There must be a constant distribution ratio K between the concentrations of these, in water and benzene.

$K = \dfrac{C_W(1-a)}{C_B(1-\beta)}$ (distribution constant) . (3)

In the concentrated solution $\beta = 1$, and is constant; $1 - a$ is also nearly equal to 1.

Find the distribution ratio of the single molecules $\frac{\text{water}}{\text{benzene}}$, from data (1) and (3).

Hence, calculate the concentration of the single molecules (in grams per litre) from datum (2), and compare the value of K_B given by the three results.

Answer (1) $K = 0{\cdot}7$.
(2) 0·7195 gram per litre in benzene.
0·5035 " " " " water.
(3) $K_B = 0{\cdot}0277,\ 0{\cdot}0279,\ 0{\cdot}0274$.

First obtain β in terms of C_W, C_B, a and K from (3);

and show that $K_B = \dfrac{[C_W(1-a)^2]}{C_B K^2 - C_W(1-a)K}$

Next, from the constancy of K_B in the cases of (1) and (3), obtain K in terms of a_1, a_3, C_W, C_{W_3}, C_B and C_{B_3}.

The value of a in each case may now be obtained from the dissociation constant. (See Problem 20, p. 189).

There are now sufficient data to calculate K. K being known, the concentration of the single molecules $C_B(1-\beta)$ may be obtained in the case (2).

Equation (1) may be transformed into :—

$$K_B = \frac{[C_B(1-\beta)]^2}{C_B - C_B(1-\beta)},$$

which allows a direct calculation of K_B from the preceding results.

67. The following formula represents the relation between the total concentration of dissolved calcium bicarbonate (less the very small amount corresponding to the solubility of $CaCO_3$) and the pressure of CO_2. If C = the concentration of the bicarbonate as grams of $CaCO_3$ per litre:

$$C = Kp^n = {\cdot}2128 \times p_{(atm.)}^{0{\cdot}37866}.$$

How many grams of $CaCO_3$ will there be in a solution in equilibrium with solid $CaCO_3$

And (*a*) CO_2 at 10 atmospheres.

(*b*) Air with 0·0504 volume percentage of CO_2?

Answer (*a*) 2·596 grams.
(*b*) 61·2 miligrams.

$$\log C = 0{\cdot}4143.$$

$$\log C = \bar{2}{\cdot}7866.$$

What is the dissociation pressure of a solution containing 0·010788 molecule of $CaCO_3$ (or gram atoms of *Ca*) per litre?

Answer **0·9841** of an atmosphere.

Schloesing ("Compt. Rend." (1872), 75, 70).

68. The absorption coefficient of oxygen in water is 0·03347, and for nitrogen is 0·01651, both at 16°. (See p. 181.)

How much oxygen and how much nitrogen can be boiled or pumped out of 1 litre of water which has been saturated (volume percentage 20 of O_2 and 80 of N_2) with air at 40 mm.?

$$Kp \text{ gas} = C \text{ (liquid)}.$$

$$\text{When } P = 1 \text{ atmosphere } K = C.$$

$$= {\cdot}03347 \text{ c.c. per c.c. of liquid.}$$

Answer $O_2 =$ **6·5** c.c.
$N_2 =$ **12·8.**

69. At 16° and 1 atmosphere, water dissolves 0·985 of its volume (reduced to N. T. P.) of carbon dioxide. The concentration of CO_2 in the water is proportional to the pressure of the gas.

Find the partition coefficient and the number of grams of CO_2 dissolved by 1 litre of water, under a pressure of 5 atmospheres.

If air saturated with water-vapour at 16° contains 0·03 per cent. of its volume of CO_2, how many gram molecules per litre of CO_2 does the water contain?

Answer **0·985, 9·58** grams per litre.
$0{\cdot}0_4130$ gram molecule per litre.

70. According to the experiments of Sieverts and Hagenacker (*Zeitsch. physikal Chem.* (1909), 68, 115), see Donnan and Shaw (*Journ. Soc. Chem. Ind.* (1910), 29, 988), oxygen dissolves in silver to the extent stated below at various pressures, the temperature being 1,075° throughout.

Find the molecular complexity of the dissolved oxygen, and the number of cubic centimetres of oxygen dissolved by 1 gram of silver exposed to the air at this temperature.

Pressure of oxygen in millimetres of mercury.	c.c. of O_2 reduced to N. T. P., dissolved by 10·87 grams of silver.
1,203	26·91
760	21·01
488	17·02

Answer The dissolved oxygen is present as O (or Ag_2O).
1 gram dissolves 0·869 c.c.

$$K = \frac{\sqrt{p}}{C} = 1{\cdot}30 \text{ (mean).}$$

Equilibrium in Solution (Heterogeneous).

71. The following ionic conductivities are stated by Kohlrausch (" Leitvermogen der Electrolyte "):

Ion =	$\frac{1}{2}\, C_2O'_4$	$\frac{1}{2}\, Ca^{\cdot}$	$\frac{1}{2}\, Sr^{\cdot}$	$\frac{1}{2}\, Ba^{\cdot}$
$L =$	63	53	54	57 (all at 18°).

The conductivities of saturated calcium, strontium and barium oxalates at 18° are: $9{\cdot}6 \times 10^{-6}$, $54{\cdot}0 \times 10^{-6}$ and $78{\cdot}3 \times 10^{-6}$.

What are the respective solubilities, in milligram equivalents per litre?

Answer 0·0828; 0·461; 0·653.

72. It will be observed that in the last calculation and l_K, l_A of the ions, in the dilute saturated solutions are taken as identical with L_A and L_K. This introduces an error, even in the case of so slightly soluble a salt as $AgCl$.

The error, of course, becomes more important, as the solubility increases.

The correction is made, by first finding approximately the saturation concentration C_S by means of the proportionality between C and κ.

Thus, if κ is the conductivity at C (known), and κ_S that at C_S,

$$C_S = 1000\eta_S = C\frac{\kappa_S}{\kappa}$$

The Λ value corresponding to this C_S may then be found by interpolation, and hence a revised value of C_S.

73. Concentrations.	Ionic conductivities.			
(1000η)	$Ag^{\cdot}$	Cl'	Λ	κ
0	55·7 (L_K)	66·1 (L_A)	121·8	0
0·0001	55·4 (l_K)	65·3 (l_A)	120·7	$12·07 \times 10^{-6}$

The conductivity of a saturated solution of $AgCl$, at 18° was $1·24 \times 10^{-6}$. What is the solubility C_S?

Answer **0·0102** milligram equivalents per litre.

Kohlrausch ("Leitvermogen der Elektrolyte").

74. The dissociation constant of orthophthallic acid is $1·2 \times 10^{-3}$, and its solubility at 17°, is 0·06 gram equivalents per litre.

What is the hydrogen ion concentration in a saturated solution of the acid at 17°, and in solutions containing 0·1, 1·0 and 5·0 c.c. of $N/NaOH$ in 10 c.c. of the solution in the presence of solid acid?

The Na salt is assumed completely dissociated.

Answer $[H^{\cdot}]$ in a saturated solution of the acid $= \mathbf{8·49 \times 10^{-3}}$.

$[H^{\cdot}]$ in the presence of $NaOH = \mathbf{7·2 \times 10^{-3}}$, $\mathbf{7·2 \times 10^{-4}}$, and $\mathbf{1·44 \times 10^{-4}}$.

(See Problem 23, p. 26.)

If C_1 is the constant concentration of the undissociated acid, C_2 the concentration of Na ($=[A']$) and $V =$ the number of cubic centimetres of normal $NaOH$ in 10 c.c. of the solution, then:

$$[A'] = \frac{V}{10}, \text{ and } [H] = \frac{KC_1 \times 10}{V}$$

Fels (*Zeitsch. Elektrochem.* (1904), 10, 208).

75. The solubility of uric acid in water at 18° is $0{\cdot}0_31506$ mol. per litre. The molecular conductivity of the saturated solution is 32·24, and the ionic conductivity of the anion L_A is 21. Find the degree of dissociation of the acid in the pure saturated solution, and the solubility in normal hydrochloric acid ($a = 0{\cdot}78$).

Answer $a =$ **0·095**,

$S =$ **0·03136** gram per litre;

the solubility being thus decreased in the ratio 0·905 to 1.

Find a from L_A and L_H (Table, p. 173), then the dissociation constant of the acid. The value of $[H^{\cdot}]$ from the HCl is then introduced into the dissociation equation, and with the constancy of $[HA]$ allows the new solubility to be calculated.

Höber ("Chemie der Zelle").

His and Paul (*Zeitsch. physiol. Chem.*) (1900), 31, 1).

76. Consider again the equilibrium between an easily and a slightly soluble acid, the latter being present also in solid form, as in the last problem, but with the difference that the dissociation constants of the two acids are of the same order.

In writing out the equations for this case, the constancy of the solubility product of the slightly soluble acid has again been assumed. Such a solution, containing saturated *a*-bromiso-cinnamic acid (HA) and unsaturated oxanilic acid (HA_1) has been investigated by Noyes.

See Van't Hoff (Lecture I., 151).

***a*-bromiso-cinnamic acid:**

$K = 0{\cdot}0144.$

Solubility before the addition of oxanilic $= C_0 = 0{\cdot}0176$.

$$\alpha_0^2 C_0 = K(1 - \alpha_0).$$

Solubility after the addition of C_1 mols. of oxanilic $= C = 0{\cdot}0135$. Degree of dissociation $= \alpha$.

Oxanilic acid (HA_1).

$$K_1 = 0{\cdot}0118.$$

Concentration of the added acid $= C_1 = 0{\cdot}0272$ mol. per litre.

Degree of dissociation in the mixture $= \alpha_1$.

Verify the following equations:

$$C_0(1 - \alpha_0) = C(1 - \alpha).$$

$$\alpha_0 = 0{\cdot}584.$$

$$(C - 0{\cdot}00732)(C - 0{\cdot}00732 + \alpha_1 C_1) = K \times 0{\cdot}00732.$$

$$\alpha_1 C_1 (C - 00732 + \alpha_1 C_1) = K_1 (C_1 - \alpha_1 C_1).$$

Hence find the concentrations of the anions of HA and HA_1.

Answer **0·0103** and **0·011** gram ion per litre.

77. It was found as above that the addition of oxanilic acid to the extent of 0·0524 mol. per litre alters the degree of dissociation of the bromiso-cinnamic to 0·390, that of the added oxanilic being 0·340.

What will now be the total amount of the bromiso-cinnamic acid in the solution?

Answer $C =$ **0·0120** mol. per litre.

$$\frac{(C_0\alpha_0)^2}{C_0(1 - \alpha_0)} = K = \frac{C\alpha(C\alpha + C_1\alpha_1)}{C(1 - \alpha)}$$

in which the denominators are equal as above.

78. The following relations hold between a relatively soluble iodide and sulphate (*e.g.*, of Na) in equilibrium with a relatively insoluble iodide and sulphate (*e.g.*, of Pb), in the presence of excess of the insoluble salts (*e.g.*, solid PbI_2 and $PbSO_4$).

$$[I']^2 \times [Pb^{\cdot\cdot}] = K[PbI_2].$$

$$[SO_4''] \times [Pb^{\cdot\cdot}] = K_1[PbSO_4].$$

Now if the salts are equally dissociated as is the case to a first approximation, $[I']$ varies as $[NaI]$; $[SO''_4]$ varies as $[Na_2SO_4]$, and the solubility products of PbI_2 and $PbSO_4$ are in the same ratio as the salt concentrations raised to the appropriate power.

	$[NaI]$	$[Na_2SO_4]$ grams in 100 c.c.
(1)	0·04151	0·01154
(2)	0·0252	0·0428

From the above concentrations of NaI and $NaSO_4$ in equilibrium with solid PbI_2 and $PbSO_4$, determine the probable ratio of the solubilities of PbI_2 and $PbSO_4$.

Answer **0·296.**

Findlay (*Zeitsch. physikal Chem.*, 34, 422).

For a homogeneous reaction in solution:

$$\Sigma\, n \log C = \log K_c = \text{constant}.$$

If one apparent mol. is really "*i*" effective mols. as judged by the lowering of the freezing point, etc., then the exponents *n* must each be multiplied by their appropriate factor *i*.

(See p. 174.)

Thus in the case of the reaction:

$$BaCO_3 + K_2SO_4 = BaSO_4 + K_2CO_3$$

(in the presence of solid $BaCO_3$ and $BaSO_4$) $n = 1$ and $i = 2{\cdot}11\,(K_2SO_4)$ and $2{\cdot}26\,(K_2CO_3)$,

$$\therefore\ C^{2\cdot11}_{K_2SO_4} = KC^{2\cdot26}_{K_2CO_3} \quad . \quad . \quad . \quad (1)$$

The active masses of $BaCO_3$ and $BaSO_4$, being constant are included in "*K*"

$$\text{or } \log C_{K_2SO_4} - 1{\cdot}07 \log C_{K_2CO_3} = \text{constant}.$$

79. The above-mentioned equilibrium was one of the earliest examples of mass action studied (Guldberg and Waage, *Journ. prakt. Chem.* (2) (1879), 19, 89).

The activity coefficients "*i*" of the two potassium salts may be taken as sensibly equal to one another. The mass equation then takes the simplest form:

A mixture of the solid barium salts in excess was treated with 1 litre of 3·5 $N.K_2CO_3$. At equilibrium 0·7 mol. of $BaSO_4$ had been transformed into $BaCO_3$.

What is the equilibrium constant $\frac{[K_2SO_4]}{[K_2CO_4]}$

Answer $K = 0·25$.

80. The mixed barium salts at the same temperature were treated with 1 litre of a solution containing 0·25 mol. of K_2SO_4 and 3·0 mols. of K_2CO_3. What is the theoretical change in the weight of the solids?

Answer **14·4** grams.

Let C_1 and C_2 be the initial concentrations of K_2SO_4 and K_2SO_3 and x the amount of K_2SO_4 transformed;

Then $$\frac{C_1 - x}{C_2 + x} \text{ or } \frac{C_1 + x}{C_2 - x} = K.$$

Hence $$x = \frac{C_1 - KC_2}{1 + K}, \text{ etc.}$$

Loss of weight $= x\,(SO_4 - CO_3)$ or $x\,(CO_3 - SO_4)$.

81. Silver nitrate and bromate are equally dissociated at the same dilution, but the latter is only soluble to the extent of 0·00810 mol. per litre. The degree of dissociation of either of them in a mixture has been taken to be the same that either would have, if present alone, at the same concentration as that of the mixture (Problem 32, p. 193).

In what follows, the degree of dissociation is calculated for the total concentration of the mixed salts, before the precipitation has taken place. If desired, a closer approximation may be obtained, by a recalculation, substituting the value of a, corresponding to the provisional concentration found in the first place.

C	a
0·0081	0·949
0·0166	0·930
0·0427	0·884

Find the weight of $AgBrO_3$ precipitated from a litre of saturated solution on the addition of 0·0085 mol. and of 0·0346 mol. of solid $AgNO_3$ (or $KBrO_3$).

$$C = -\frac{C_1}{2} + \sqrt{\frac{C_0{}^2 a_0{}^2}{a^2} + \frac{C_1{}^2}{4}} = 0{\cdot}00510 \text{ and } 0{\cdot}00216.$$

Where a_0 is the degree of dissociation of saturated $AgBrO_3$, a the common degree of dissociation of each salt after the addition of $AgNO_3$; C_0 and C the saturation concentrations of $AgBrO_3$, before and after the addition, and C_1, the concentration of the added $AgNO_3$.

Answer $0{\cdot}00810 - 0{\cdot}0051 = 0{\cdot}003 \times 236 = \mathbf{0{\cdot}708}.$
$0{\cdot}00810 - 0{\cdot}00216 = 0{\cdot}00594 \times 236 = \mathbf{1{\cdot}40}.$

82. What weight of $AgBrO_3$ is precipitated when 300 cubic centimetres of a 0·0577 molar normal solution of $KBrO_3$ is added to 200 cubic centimetres of a saturated solution of $AgBrO_3$?

Answer **0·72** gram.

C before precipitation

$$= \frac{0{\cdot}0081 \times 4 + 0{\cdot}0577 \times 6}{10} = 0{\cdot}0378.$$

83. A solution 3·0 N. with respect to KOH, when shaken with excess of moist $AgOH$ and $AgCl$ was found at equilibrium to contain 3·503 millimols per litre of KCl, and 356·8 millimols of KOH; while a solution initially 0·1 N. to KOH and 0·5 N. to KCl, with the same solid phases gave 0·918 millimol of KCl, and 94·4 of KOH. The degrees of dissociation of KCl and KOH being 90 per cent. and 84 per cent. respectively in the first, and 94 and 88 per cent. in the second case, find the solubility product of $AgOH$, if that of $AgCl$ is $1{\cdot}5 \times 10^{-5}$ mols. per litre (assuming complete dissociation of $AgOH$). Also, if the total solubility of $AgOH$ is found directly to be $2{\cdot}16 \times 10^{-4}$, find the amount of undissociated $AgOH$ in equilibrium with solid $AgOH$, and, hence, the limiting solubility in the presence of excess of concentrated alkali.

$$[Ag^{\cdot}] \times [OH'] = K_1[AgOH] = [Ag^{\cdot}]^2$$
$$[Ag^{\cdot}] \times [Cl'] = K_2[AgCl] = [Ag^{\cdot}]^2;$$

$[Ag^{\cdot}]^2$ referring to the concentration of the $Ag^{\cdot}$ ions from $AgOH$ and $AgCl$ in pure water.

$$\frac{Ag^{\cdot}(\text{from } AgOH)}{Ag^{\cdot}(\text{from } AgCl)} = \sqrt{\frac{OH}{Cl}}$$

Answer Solubility product,

$$[Ag^{\cdot}] \times [OH'] = 1{\cdot}47 \times 10^{-4} \text{ mols. per litre.}$$

∴ undissociated $AgOH$, and solubility in the presence of excess of $OH' = 0{\cdot}7 \times 10^{-4}$.

$$\text{For } C_{Ag} (\text{from } AgOH) = \frac{1{\cdot}5 \times 10^{-5}}{\sqrt{0{\cdot}01045}}$$

$$\text{Since} \quad \left.\begin{aligned} C(Cl') &= 0{\cdot}01052 \\ C(OH') &= 0{\cdot}01038 \end{aligned}\right\} 0{\cdot}01045.$$

Noyes (*Zeitsch. physikal Chem.* (1903), 42, 336).

84. $CaCO_3 + H_2O = \frac{1}{2} CaHCO_3 + \frac{1}{2} Ca(OH)_2$.

The saturated solution of $CaCO_3$ contains $13{\cdot}1 \times 10^{-5}$ milligram atoms of total Ca per litre;

$$K_3 = \frac{H \times CO''_3}{HCO'_3} = 1{\cdot}295 \times 10^{-11}$$

and $\quad K_w = 0{\cdot}55 \times 10^{-14}$ (all at 16°).

What is the percentage hydrolysis of the $CaCO_3$?

(See Problem 48, p. 198.)

Answer 80 per cent.

$$\frac{H^{\cdot} \times CO''_3}{HCO'_3} = \frac{CO''_3 \times 0{\cdot}55 \times 10^{-14}}{(HCO'_3)^2} = K_3.$$

CO''_3 = (Total mols. of $CaCO_3$ dissolved) — (mols. of HCO'_3). Hence $[HCO_3] = 10{\cdot}51 \times 10^{-5}$ gram molecules by substitution for CO''_3 in the above equation.

85. A solution in equilibrium with solid $CaCO_3$ contains 10·66 milligram equivalents of total Ca per litre, when the CO_2 pressure is 0·1422 atmosphere, and 21·72 milligram equivalents when the CO_2 pressure is 0·9841 atmosphere. The calcium is dissolved chiefly as $Ca\,(HCO_3)_2$ and its ions.

The degrees of dissociation by analogy with Ca salts of other univalent anions are 0·87 and 0·83 respectively. Find the concentration of HCO'_3 ions, the solubility product $Ca^{\cdot\cdot} \times CO_3$, and the solubility of $CaCO_3$ in pure water.

$$[Ca^{\cdot\cdot}] \times [CO''_3] = K_1[CaCO_3] \quad . \quad . \quad (1)$$

$$[H^{\cdot}] \times [HCO'_3] = K_2[H_2CO_3] \quad . \quad . \quad (2)$$

$$[H^{\cdot}] \times [CO''_3] = K_3[HCO'_3] \quad . \quad . \quad (3)$$

$$[H_2CO_3] = K_4 p_{CO_2} \quad . \quad . \quad . \quad (4).$$

From (2) and (3) $K_2\,[H_2CO_3]\,[CO''_3] = K_3\,[HCO'_3]^2$ (5)

„ (5) „ (1) $K_1\,K_2\,[H_2CO_3] = K_3\,[HCO']^2\,[Ca^{\cdot\cdot}]$

and $[Ca^{\cdot\cdot}] = \frac{1}{2}\,[HCO'_3]$ (in gram ions).

Since the dissolved carbonate is negligible compared to the bicarbonate

$$\therefore\ 2\,K_1\,K_2\,[H_2CO_3] = K_3\,[HCO'_3]^3.$$

$$\text{or with (4) } 2\,K_1\,K_2\,K_4\,[p_{CO_2}] = K_3\,[HCO_3]^3.$$

$$K_2 = 3{\cdot}04 \times 10^{-7}$$

$$K_3 = 1{\cdot}295 \times 10^{-11}$$

$$K_4 = 0{\cdot}04354$$

(See Problem 18, p. 188.)

(1) Answer $HCO_3 =$ **0·009272** and

$$\sqrt[3]{K_1} = \frac{[HCO'_3]}{12{\cdot}69 \times \sqrt[3]{p_{CO_2}}} = 0{\cdot}001428.$$

(2) Answer Mean $K_1 = \mathbf{2{\cdot}842 \times 10^{-9}}$.

(3) Answer **5·333** milligrams of $CaCO_3$.

$$\text{For } \sqrt[3]{K_1} = \sqrt[3]{\frac{K_3}{2\;K_2K_4}} \times \frac{HCO_3}{\sqrt[3]{p_{CO_2}}} = 0{\cdot}00140, \text{ etc.}$$

$$Ca \times CO_3 = K_1\,[CaCO_3] = \sqrt[3]{K_1} \text{ mgm. mols.}$$

$$= 0{\cdot}0000533 \text{ gram ion.}$$

$$= 5{\cdot}333 \text{ milligrams of } CaCO_3.$$

Bodländer (*Zeitsch physikal Chem.* (1900), 35, 25).

86. According to Schloesing the solubility of $CaCO_3$ (total) in pure water is 13·1 milligrams per litre. Calculate the percentage of the hydrolysis

$$CO''_3 + H_2O = (OH') + HCO'_3$$

which must exist in order that this experimental solubility should agree with the solubility product $Ca \times CO_3$ of the last problem.

$$CO''_3 = \frac{[Ca^{\cdot\cdot}] \times [CO''_3]}{[Ca^{\cdot\cdot}]}$$

CO''_3 converted into $HCO'_3 = (13{\cdot}1 - 2{\cdot}17) \times 10^{-5}$.

Answer Percentage hydrolysis = **83·4**.

87. The second dissociation constant of H_2CO_3 (K_3 above) is, according to McCoy (*Journ. Amer. Chem. Soc.*, April, 1911) $5{\cdot}5 \times 10^{-11}$. Taking the solubility of $CaCO_3$ as roughly 10 milligrams per litre (hydrolysed or not), calculate to a first approximation the degree of hydrolysis of $CaCO_3$ in pure water, and the concentration of OH produced. (A more exact method of calculation will be found in the paper referred to). $K_w = 0{\cdot}54 \times 10^{-14}$.

Answer 62 per cent. hydrolysed, $[OH'] = 6 \times 10^{-4}$.

$$\frac{[H^{\cdot}] \times [CO''_3]}{[HCO'_3]} = K_2 = \frac{[H^{\cdot}] \times (1-\beta)C}{\beta C} = \frac{K_W \times (1-\beta)C}{(\beta C)_2}$$

$$\frac{0{\cdot}54 \times 10^{-14} \times (1-\beta)}{\beta^2 \times 1 \times 10^{-4}} = 5{\cdot}5 \times 10^{-11}.$$

88. At a partial pressure of $CO_2 = 0{\cdot}1417$ atmosphere, $Ba\ (HCO_3)_2$ is soluble to the extent of 9·286 milligram equivalents to the litre, and dissociated to 88 per cent. If the actual solubility of $BaCO_3$ is $9{\cdot}42 \times 10^{-5}$ in water free from CO_2, find the $[OH']$ concentration of this saturated solution.

Answer $[OH'] = 7{\cdot}37 \times 10^{-5}$.

(See last problem and Bodländer, *loc. cit.*, Problem 85.)

Find $\sqrt[3]{K_1}$, CO''_3 and HCO'_3 as before, and hence the degree of hydrolysis.

89. The total solubility of $NaHCO_3$ is governed by the equations:

$$[H^{\cdot}] \times [HCO'_3] = 3{\cdot}04 \times 10^{-7}\ [H_2CO_3] \quad . \quad (1)$$
$$[H^{\cdot}] \times [CO''_3] = 1{\cdot}3 \times 10^{-11}\ [HCO'_3] \quad . \quad (2)$$
$$[H_2CO_3] = 0{\cdot}04955\ [CO_2] \quad .. \quad . \quad (3)$$

Hence prove the relation:

$$[HCO_3]^2 = [\tfrac{1}{2}\ CO''_3] \times p_{CO_2} \times 1159 \quad . \quad . \quad . \quad (4)$$

Bodländer (*loc. cit.*).

It has been found that $NaHCO_3$ is less soluble in the presence of excess of CO_2 than it is in equilibrium with air. The actual values at certain temperature are:

1·09, in equilibrium with pure CO_2, at atmospheric pressure.

1·48, in equilibrium with air containing 0·04 per cent. of CO_2.

The solubilities are expressed in gram ions of *Na* per litre.

The dissolved $NaHCO_3$ in the first case is 65 per cent. dissociated ($100a$). Assume as usual that the concentration of the undissociated $NaHCO_3$ in equilibrium with the solid is the same in both cases.

(1) Find $[HCO_3]$ in the first case, previously proving that $[CO''_3]$ is small compared to $[HCO'_3]$.

(2) Find $[HCO_3]$ in the second case, also the volume of CO_2 (at N. T. P.) which will be given off by a litre of the solution saturated at $p_{CO_2} = 1$ atmosphere, when air is subsequently drawn through the solution.

Answer $[HCO'_3] = 0{\cdot}7$ gram ion per litre.
$[CO''_3] = 0{\cdot}00043$ „ „ „ „
$[CO''_3] = 0{\cdot}29$.
CO_2 given off $= 65$ litres.

(1) $[HCO'_3]$ in the first case is obtained to a first approximation from a and C; then CO_3 is obtained from equation (4).

(2) Total salt = total ions + undissociated salt (constant).

$$\text{Total ions} = [HCO'_3] + [\tfrac{1}{2}\,CO''_3]$$

$$\therefore\ [HCO'_3]^2 = (\text{ions} - HCO_3)\,p_{CO_2} \times 1159.$$

$$2\,HCO'_3 = H_2O + CO_2 + CO''_3.$$

∴ each gram ion of CO''_3 formed from HCO'_3 gives 1 mol. of gaseous CO_2.

In the first case:

$$aC = [HCO'_3] = 0{\cdot}7.$$

$$[CO''_3] = \frac{0{\cdot}49}{1{,}159 \times 1} = 0{\cdot}003.$$

$$1 - a = NaHCO_3 = 0{\cdot}38.$$

In the second case:

$$[CO''_3]\ (\text{equivalents}) = [\tfrac{1}{2}\,CO''_3].$$

$$[\tfrac{1}{2}\,CO''_3] = \text{Total concentration} - \text{undissociated salt} - [HCO'_3].$$

Substituting in equation (4), and solving for $[HCO_3]$.

$$[HCO_3] = 0{\cdot}52.$$

$$[\tfrac{1}{2}\,CO''_3] = 1{\cdot}1 - 0{\cdot}52 = 0{\cdot}58.$$

$$[CO''_3] = 0{\cdot}29.$$

90. The solubility of $AgCl$ is increased by the addition of ammonia. This is due to the formation of a complex $(AgCl)_m$ and $(NH_3)_{m+1}$, similar to those formed in the dry way by passing NH_3 over $AgCl$.

The amounts of ammonia and silver chloride in the solution are regulated by the following equilibria.

Let C be the concentration and a the degree of dissociation of the complex salt.

$$[NH_3]^{m+1}[AgCl]^m = K_1C(1 - a) \quad . \quad (1)$$

$$[Cl]^m\,[(Ag)_m\,(NH_3)_{m+1}] = K_2C(1 - a) \quad . \quad (2)$$

$$[Ag]^m\,[NH_3]^{m+1} = K_3[(Ag)_m\,(NH_3)_{m+1}] = K_3{\cdot}aC \quad (3)$$

$$p_{NH_3} = K_4\,[NH_3] \quad . \quad . \quad . \quad (4)$$

$$\text{From (2)}\ (aC)^{m+1} = K_2\,(1 - a)\,C \quad . \quad (5)$$

$$\text{From (1)}\ [NH_3]^{m+1} = K_1\,\frac{C(1 - a)}{[AgCl]^m} \quad . \quad (6)$$

But $[AgCl]$ and therefore $[AgCl]^m$ are constant in the presence of solid $AgCl$.

Therefore from (5) and (6)

$$[NH_3]^{m+1} = K'(1 - a)C = K''(aC)^{m+1}.$$

i.e., the concentration of NH_3 is proportional to the concentration of the complex kation. This has been shown to be the case, giving a justification for the general formula assumed above. It remains therefore to determine the value of m. This may be done by varying $[Cl]$, *e.g.*, by adding KCl.

Let the degree of dissociation of the added KCl be the same as that of the complex salt.

Substituting $[Ag]$ in equation (3) by means of the relation:

$$[Ag] \times [Cl] = K.$$

$$K'_3\,aC = \frac{[NH_3]^{m+1}}{(a[KCl])^m}$$

and

$$\sqrt{K'_3} = \frac{[NH_3]^{\frac{m+1}{2}}}{C^{\frac{1}{2}}\,a^{m+\frac{1}{2}}\,[KCl]^m} \quad . \quad . \quad (7)$$

The total ammonia present may be determined in the usual manner.

This total is made up (1) of complex ammonia (the amount of which is known from the $AgCl$ dissolved); (2) of NH_4OH; (3) of NH_3, the concentration of which is required as one of the data.

The partial pressure of gaseous ammonia, the concentration of total ammonia dissolved (excluding complex) and the concentration of NH_3 are connected by the following relation:

$$\frac{p(NH_3)}{12{\cdot}69} = [NH_3]$$

$$= [NH_3 + NH_4OH]\,(1 + 0{\cdot}033\,[NH_3 + NH_4OH]) \; . \quad (8)$$

From the following experimental data, by means of equations (7) and (8), determine:

(*a*) The value of $\sqrt{K}$ with the various values of m.

Therefore (*b*) The formula of the complex.
(*c*) The partial pressures of NH_3 over the solutions.

Total ammonia	$AgCl$	KCl	a
0·7522	0·04758	0	0·89
0·7497	0·0333	0·0511	0·86

All concentrations in mols. per 1,000 grams of water.

Answer (*a*) $\sqrt{K} = 15{\cdot}87$ and $15{\cdot}71$ when $m = 1$.
66·7 ,, 49·4 ,, $m = 2$.
(*b*) $AgCl \cdot 2\,NH_3$.
(*c*) 8·5 and 8·9 millimetres.

Bodländer (*Zeitsch. physikal Chem.* (1902), 39, 598).

91. It is often possible to elucidate the equilibrium between a dissolved substance and its ions, by means of the distribution ratio of the undissociated substance between the aqueous and non-aqueous solvents.

Thus the equilibrium between a mercuric halide HgX_2 and the halogen ion X' with which it forms complexes may be represented by:

$$K_1 = \frac{[(HgX_2)_m(X')_n]}{[HgX_2]^m\,[X']^n}$$

$[HgX_2]$ is found by the distribution ratio $[X']$ from the concentration of RX, *i.e.*, the alkali halide not required to form the complex salt.

In the case of the $HgCl_2KCl$ complex salt (Sherrill) a considerable percentage of $HgCl_2$ is present in the free state.

By altering the concentrations of the reacting substances, and by trial of various values of m and n, those may be found which give a constant product K_1 as above. It was thus determined that $m = 1$ and $n = 2$ for the concentrations stated below.

Distribution Ratio.

An aqueous solution of $HgCl_2$ (which is undissociated) containing 0·263 gram in a given volume, is in equilibrium with a benzene solution, containing 0·0197 gram in the same volume.

At a total concentration of 0·25 mol. KCl and 0·0665 mols. $HgCl_2$, the C_6H_6 concentration of $HgCl_2$ was 0·00147.

And at a concentration of 0·125 mol. KCl, and 0·0384 mol. $HgCl_2$ the $HgCl_2$ in C_6H_6 was 0·001671.

Find the value of K above.

Answer **98·55 82·58.**

For, if "C" is the concentration of $HgCl_2$ in the complex, "b" the concentration of the free $HgCl_2$ and "a" the total original concentration of the alkali halide:

$$K = \frac{\frac{C}{m}}{b^m\left(a - \frac{n}{m}C\right)^n} = \frac{C}{b(a - 2C)^2}$$

Distribution ratio $= 13·4$.

(1) $C = 0·0665 - 13·4 \times 0·00147 = 0·0468$.
$b = 0·0197$.
$a - 2C = 0·25 - 2 \times 0·0468$.

(2) $C = 0·0160 \quad b = 0·0224$.
$a - 2\,C = 0·125 - 2 \times 0·0160$.

92. The concentration of I' in a mixed solution of KI and HgI_2 has been found by its influence on the catalysis of H_2O_2 (Bredig and Walton, Abegg Handbuch II., 2, 650).

The concentration of KI being 0·03125 gram molecule, that of I', 0·1094, and that of HgI_2, 0·1315, find the simplest formula for the complex salt by means of the ratio $\frac{n}{m}$, if all the HgI_2 is present as complex:

Answer $\frac{n}{m} = \mathbf{1·54}$.

The formula of the complex salt is $K_3Hg_2I_7$.

The anion is $\{(HgI_2)_2(I)_3\}'''$.

$$\text{Since } \frac{\text{mols. } I \text{ in complex}}{\text{mols. } HgI_2 \text{ in complex}} = \frac{n}{m}.$$

93. If the reaction by means of which the complex $(HgX_2)_m(X)_n$ anion is formed, is supposed to take place between the ions $Hg^{\cdot\cdot}$ and X', then:

$$mHg + (2m + n)X' \rightleftarrows (HgX_2)_m(X')_n$$

$$K = \frac{[(HgX_2)_m(X')_n]}{[Hg]^m[X']^{2m+n}}.$$

Or, if C is the concentration of HgI_2 (assumed practically all present as complex) and a is the total halogen, then:

$$K = \frac{\dfrac{C}{m}}{[Hg]^m\left(a - \dfrac{nc}{m}\right)^{2m+n}} \quad . \quad . \quad (1)$$

And for two solutions of different compositions:

$$\frac{[Hg^{\cdot\cdot}]_1}{[Hg^{\cdot\cdot}]_2} = \left\{\frac{[(HgX_2)_m(X')_n]_1 \times [X']_2{}^{2m+n}}{[(HgX_2)_m(X')_n]_2[X']_1{}^{2m+n}}\right\}^{\frac{1}{m}}$$

$$= \left\{\frac{\dfrac{C_1}{m}\left(a_2 - \dfrac{nC_2}{m}\right)^{2m+n}}{\dfrac{C_2}{m}\left(a_1 - \dfrac{nC_1}{m}\right)^{2m+n}}\right\}^{\frac{1}{m}} \quad . \quad . \quad (2)$$

The ratio of $[Hg^{\cdot\cdot}]$ may be found from E. M. F. measurements as on p. 234.

Bodländer found the values of the constant mentioned above, first having determined the values of m and n.

Thus the E. M. F. of $Hg \left| \begin{matrix} 1\ N.\ KI \\ 0{\cdot}00454\ HgI_2 \end{matrix} \right| \begin{matrix} 1\ N.\ KI \\ 0{\cdot}00227\ HgI_2 \end{matrix} \Big| Hg$

was 0·0085 volt. Find m.

Note that C_2 and C_1 are here small compared to a.

$$\text{Answer} \quad m = \frac{0{\cdot}0295}{0{\cdot}0085 \log 2} = \mathbf{1{\cdot}04}.$$

94. If $m = 1$ and $n = 2$ the value of K was found to remain constant through a considerable range of concentrations. Thus a solution containing $a\ (KI) = 0{\cdot}50$ and $C\ (HgI_2) = 0{\cdot}0891$ was found by measurement against a normal electrode to have $[Hg^{\cdot\cdot}] = 3{\cdot}7 \times 10^{-30}$. (See "Electromotive Force," p. 237.)

A mercury electrode in a solution with $a = 0{\cdot}125$ and $C = 0{\cdot}0223$, was 0·053 volt positive to one in the former solution. Find the $[Hg^{\cdot\cdot}]$ in the second solution and the constant of the complex formation, as in equation (1). $t = 25°$.

$$\text{Answer}\quad [Hg^{\cdot\cdot}] = \mathbf{2{\cdot}3 \times 10^{-28}}.$$
$$K = \mathbf{2{\cdot}2 \times 10^{-30}}.$$

$$\text{For } K = \frac{0{\cdot}0891}{3{\cdot}7 \times 10^{-30} \times (0{\cdot}50 - 2 \times 0{\cdot}0891)^4}$$

$$\log \frac{[Hg^{\cdot\cdot}]}{[Hg^{\cdot\cdot}]} = \frac{0{\cdot}0530}{0{\cdot}0295}$$

$$\log [Hg^{\cdot\cdot}] = \overline{28}{\cdot}37.$$

A full discussion of these and other results may be found in an article by Ley, Quecksilber ("Handbuch der Anorg. Chem." II. 2, Abegg).

Solution Equilibrium and Temperature.

95. Find the heat of solution of CO_2 at constant pressure and constant volume, in water at 20°, if the solubility is 0·8928 at 20°, and the temperature coefficient of the solubility = — 0·02483 per 1° rise.

$$Q_p = \frac{RT^2dC}{C} = -4{,}700.$$

Add RT.

Answer + **4,100** cal. evolved by solution at constant volume;
4,700 „ „ „ „ pressure.

96. The heat of solution of a slightly soluble substance may be calculated from the change of the saturation concentration with temperature, in the same way that the inner heat of vaporisation of a condensed substance may be calculated from the change of concentration in the gaseous phase (see Problem 36, p. 161).

At $T_1 = 273$ the solubility of succinic acid is 2·88.

At $T_2 = 281{\cdot}5$ the solubility of succinic acid is 4·22.

What is the molecular heat of solution ?

Answer — 6,900 calories (heat is absorbed).

$$\log C_2 - \log C_1 = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

97. As in the case of the corresponding calculation for a vaporisation, Q refers to the formation of one effective gas molecule, as defined by Avogadro's Law, so, for a dilute solution, a simultaneous determination of the heat of solution of a known weight allows conclusions to be drawn as to the dissociation or association of the simplest formula molecule. The symbol "i" has been proposed by Van't Hoff for the number of effective gas or dissolved molecules derived from one formula weight. (See p. 174.)

Thus in the case of N_2O_4 dissociated to a degree of a.

$$i = 1 - a + 2\,a = 1 + a.$$

And for a salt completely dissociated electrolytically into two ions

$$i = 2.$$

98. The solubilities of oxalic acid at $t = 0°$ C. and $t = 10°$ C. are 5·2 and 8·0 respectively.

Find "i," if the heat of solution of 1 gram at 5° is — 91·1 calories.

Find Q for 1 mol. in solution as above, in the case of succinic acid, and compare with the directly determined value of Q for 1 formula weight.

Answer $i = 1{\cdot}25$.

99. The heat of solution of 1 formula weight of $HgCl_2$ at 30° C. is — 2,700 calories. If the solubilities are 6·57 and 11·84 at 10° and 50°, calculate the apparent value of R for 1 formula weight of dissolved $HgCl_2$, and hence its formula in solution.

Answer $R = 2 \therefore HgCl_2$ exists in solution as simple molecules.

$$R = \frac{Q \times (T_1 - T_2)}{2{\cdot}303 \times T_1 \times T_2\,(\log C_1 - \log C_2)}.$$

100. In the case of $Ca(OH)_2$, at $t_1 = 15^\circ\cdot6$ $C_1 = 0\cdot129$; at $t_2 = 54\cdot4$ $C_2 = 0\cdot103$, and the value of i is 2·59. What is the "last" heat of solution of 74 grams of slaked lime at 35°? (See p. 29.)

Answer $Q = +$ **2,800** calories.

$$Q = \frac{i \,.\, RT_1T_2}{T_2 - T_1} \cdot \log \frac{C_2}{C_1}.$$

101. The solubility of $BaSO_4$ at 18°·4 is 1 mol. in 50,055 litres, and at 37°·7 is 1 mol. in 37,282 litres. What is the heat of formation of 1 mol. of the solid salt from its ions?

Answer + **5,500** calories.

Van't Hoff (Hollemann).

ELECTROMOTIVE FORCE AND CHEMICAL AFFINITY.

Electrical and Chemical Energy.

The electrical work of a reversible reaction occurring at electrodes may be substituted for A in the fundamental equation (1):

$$A - Q = q.$$

If the electromotive force E be measured in volts, the quantity of electricity in coulombs, and the amount of chemical action in equivalents, then, for each equivalent transformed F coulombs of electricity pass, and

$$EF = q + Q$$

$+ q$ is the decrease of chemical energy for each equivalent transformed, and may be measured as the calorimetric heat evolved by the chemical reaction, carried out at constant volume.

$+ Q$ is the reversible heat absorbed. The heat must of course be expressed in the same units as EF.

Substituting in the combined fundamental equation (1 and 2)

$$EF = q + FT\frac{dE}{dt} \quad . \quad . \qquad (1)$$

(See introductions to former sections).

A simple arrangement can be imagined and has been actually used, which permits of the measurement of these separate quantities of energy. A completely reversible cell is immersed in a calorimeter, the conductor which connects its electrodes being placed in another calorimeter.

If the circuit has a very high, and in the limit, an infinite resistance, the electrical energy will be completely converted into heat in calorimeter (2). The heat evolved in (2) is $+ A$. When the cell is working, calorimeter (1) loses or gains heat from the cell. The loss, heat absorbed by the cell in (1) is $+ Q$.

The combined evolution of heat in the two calorimeters is equal to $+ q$, and to the loss of chemical energy in the cell.

Electromotive Force and Concentration.

The conception of osmotic pressure supplies a method of representing the maximum work associated with reactions in solutions. (See p. 89.)

Since the maximum work of a given reaction must be the same in whatever terms it is described, equations may be found which connect the electromotive force of a cell with the osmotic pressures and the concentrations of the active molecules.

Thus, if there are E volts between two electrodes on open circuit, nF coulombs of current are taken out of the cell and 1 molecule is reduced from the osmotic pressure P_1 to P_2.

$$nEF = RT \log \frac{P_1}{P_2}.$$

The osmotic pressures may be expressed as the concentrations C_1 and C_2, to which they are proportional;

and $$E = \frac{RT}{nF} \log \frac{C_1}{C_2} \quad . \quad . \qquad (2)$$

where n are the number of faradays given or taken up by the molecule in question (*i.e.*, the valency).

If the solutions surrounding the two electrodes are in contact with one another, there is also, in general, a diffusion potential e_d at the surface of separation.

For a binary electrolyte (such as $AgNO_3$):

$$e_d = \frac{RT}{F} (2v_A - 1) \log \frac{C_1}{C_2} \quad . \qquad (3)$$

v_A = transport number of the anion.

$$\therefore E \text{ (with ionic migration)} = \frac{RT}{F} 2v_A \log \frac{C_1}{C_2} \quad . \qquad (4)$$

Multivalent Ions and Rule as to Signs.

If E is measured as the positive potential of the electrode in C_1 minus the positive potential of the electrode in C_2, and if the current-giving process is the discharge of kations at the former and their formation at the latter electrode, then, if $C_1 > C_2$, E is positive and:

$$E = \frac{RT}{n_K F} \log \frac{C_1}{C_2} \quad . \quad . \qquad (5)$$

gives correctly the sign of E.

Conversely, if the electrodes are reversible with respect to the anion, and the other conditions are the same as those laid down above:

$$E = -\frac{RT}{n_A F} \log \frac{C_1}{C_2} \quad . \quad . \qquad (6)$$

the electrode in C_1 now having the higher negative potential.

In order to obtain the E. M. F. with migration, the diffusion E. M. F. e_d must be added in each case:

$$2\,v_A - 1 = 1 - 2\,v_K.$$

$$E\ (\text{with migration}) = \frac{RT}{n_A F}\,2\,v_K \log\frac{C_1}{C_2} \quad . \qquad (7)$$

for anion reversible electrodes (binary electrolyte).

If the ions have valencies n_A, n_K, it can be shown:

$$= \frac{RT}{F}\,\frac{\dfrac{U_A}{n_A} - \dfrac{U_K}{n_K}}{U_A + U_K}\log\frac{C_1}{C_2} \quad . \quad . \qquad (8)$$

The weaker solution has the sign of the more mobile ions.

Thus, if, in this case, the electrodes are reversible with respect to the kation, and if $\dfrac{U_A}{n_A} > \dfrac{U_K}{n_K}$ and $C_1 > C_2$, then e_d is positive and increases E, because the C_2 solution is negative to the C_1 solution.

Therefore:

$$E\ (\text{with migration}) = \frac{RT}{F}\log\frac{C_1}{C_2}\left(\frac{1}{n_K} + \frac{\dfrac{U_A}{n_A} - \dfrac{U_K}{n_K}}{U_A + U_K}\right)$$

$$= \frac{RT}{F}\,\frac{n_A + n_K}{n_A \times n_K}\,\frac{U_A}{U_A + U_K}\log\frac{C_1}{C_2} \quad . \qquad (9)$$

But, if n_A and n_K are expressed in terms of the highest valent ion (*e.g.*, in the case of $K_4Fe(CN)_6$, n_A of $[Fe(CN)_6]''''$ $= 1$ and n_K of $K = \frac{1}{4}$), then $\dfrac{n_A + n_K}{n_A n_K} = i =$ number of mols. at complete dissociation (*e.g.*, for $AlCl_3$ $i = \dfrac{\frac{1}{3} + 1}{\frac{1}{3} \times 1} = 4$).

Hence

$$E = \frac{RT}{F}\,i\,v_A \log\frac{C_1}{C_2} \quad . \quad . \quad . \quad . \qquad (10)$$

Single Potential and Reaction Potential.

The total E. M. F. without migration is made up of:

$$\left.\begin{array}{ll}\left.\begin{array}{r}\text{Kation}\\ \text{reversible}\end{array}\right\} & e_1 = + \frac{RT}{n_K F} \log \frac{C_1}{c} \\ & \qquad\qquad \text{and } - e_2 = - \frac{RT}{n_K F} \log \frac{C_2}{c} \\ \left.\begin{array}{r}\text{Anion}\\ \text{reversible}\end{array}\right\} & e_1 = \frac{RT}{n_A F} \log \frac{C_1}{c} \\ & \qquad\qquad \text{and } - e_2 = + \frac{RT}{n_A F} \log \frac{C_2}{c} \end{array}\right\} \quad (11)$$

Thus, for electrodes reversible with respect to kations which possess different valencies n_1 and n_2:

$$E = e_1 - e_2 = \frac{RT}{F}\left(\frac{1}{n_1} \log \frac{C_1}{c_1} - \frac{1}{n_2} \log \frac{C_2}{c_2}\right). \qquad (12)$$

And for one electrode reversible with respect to the kation, and one with respect to the anion:

$$E = \frac{RT}{F}\left(\frac{1}{n_K} \log \frac{C_1}{c_K} + \frac{1}{n_A} \log \frac{C_2}{c_A}\right). \qquad (13)$$

Calling the terms $-\frac{RT}{n_K F} \log c_K$ or $-\frac{RT}{n_A F} \log c_A$ the normal potentials e_0 of the ion-forming material in question, we have for the “single potentials (e_K, e_A) of the kation—and anion—reversible electrodes in C normal solutions of their respective ions:

$$\left.\begin{array}{l} e_K = e_{OK} + \frac{RT}{n_K F} \log C_K \\ e_A = e_{OA} + \frac{RT}{n_A F} \log C_A \end{array}\right\} . \qquad (14)$$

(n_A F the charge in coulombs carried by one gram anion is taken as negative).

All measurements of E are referred to a platinum electrode saturated with H_2, at atmospheric pressure and dipping into a normal solution of hydrogen ions.

The single potential (e) of any electrode is then the total E. M. F. of the electrode, measured against a normal hydrogen electrode.

For the single potential of any other oxidation or reduction process occurring reversibly at an electrode, we have quite similarly:

$$e = \frac{RT}{nF}(\Sigma n \log C - \log K). \qquad (15)$$

nF being the number of faradays concerned, and C the concentrations of the reacting molecules.

$$\text{And } e = e_0 + \frac{RT}{nF}(\Sigma n \log C_{OX} - \Sigma n \log C_{red}). \qquad (16)$$

C_{OX} being the concentration of the molecules in the higher, and C_{red} in the lower degree of oxidation. Thus

$$e\,(Fe^{\cdots} \longrightarrow Fe^{\cdot\cdot}) = e_0\,(Fe^{\cdots} \longrightarrow Fe^{\cdot\cdot}) + \frac{RT}{F}\log\frac{C\,(Fe^{\cdots})}{C\,(Fe^{\cdot\cdot})}$$

List of Normal Potentials.

(Abhandl. d. Deutsch. Bunsen Gesellschaft, 1911, 5.)

The less accurate values are marked with an asterisk.

Kation formation.		*Anion discharge.*	
$K \longrightarrow K^{\cdot}$	− 3·2*	$S'' \longrightarrow S$ (solid)	− 0·55
$Na \longrightarrow Na^{\cdot}$	− 2·8*	$4OH' \longrightarrow O_2 + 2H_2O$	+ 0·41
$Mg \longrightarrow Mg^{\cdot\cdot}$	− 1·55	$2I' \longrightarrow I_2$ (solid)	+ 0·54
$Zn \longrightarrow Zn^{\cdot\cdot}$	− 0·76	$2Br' \longrightarrow 2Br$ (liquid)	+ 1·08
$Fe \longrightarrow Fe^{\cdot\cdot}$	− 0·43	$2Cl' \longrightarrow Cl_2$ (gas)	+ 1·35
$Cd \longrightarrow Cd^{\cdot\cdot}$	− 0·40	$2F' \longrightarrow F_2$ (gas)	+ 1·9*
$Tl \longrightarrow Tl^{\cdot}$	− 0·32		
$Co \longrightarrow Co^{\cdot\cdot}$	− 0·29		
$Ni \longrightarrow Ni^{\cdot\cdot}$	− 0·22		
$Pb \longrightarrow Pb^{\cdot\cdot}$	− 0·12		
$Sn \longrightarrow Sn^{\cdot\cdot}$	− 0·10		
$H_2 \longrightarrow 2H^{\cdot}$	∓ 0·00		
$Cu \longrightarrow Cu^{\cdot\cdot}$	+ 0·34		
$Ag \longrightarrow Ag^{\cdot}$	+ 0·80		
$Hg \longrightarrow Hg^{\cdot\cdot}$	+ 0·86		
$Au \longrightarrow Au^{\cdot}$	+ 1·5*		

Oxidations.

$H_2 + 2OH' \longrightarrow 2H_2O \quad - 0{\cdot}82$

$2H_2O \longrightarrow O_2 + 4H^{\cdot} + 1{\cdot}23$

$Cr^{\cdot\cdot\cdot} + 4H_2O \longrightarrow HCrO_4 + 7H^{\cdot} + 1{\cdot}3$

$Mn^{\cdot\cdot} + 2H_2O \longrightarrow MnO_2 + 4H^{\cdot} + 1{\cdot}35$

$Pb^{\cdot\cdot} + 2H_2O \longrightarrow PbO_2 + 4H^{\cdot} + 1{\cdot}44$

$MnO_2 + 2H_2O \longrightarrow MnO'_4 + 4H^{\cdot} + 1{\cdot}63$

$O_2 + H_2O \longrightarrow O_3 + 2H^{\cdot} + 1{\cdot}9$

Change of Valency, Ionic Charge.

$Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} \quad + 0{\cdot}17$

$Fe(CN)_6'''' \longrightarrow Fe(CN)_6''' \quad + 0{\cdot}40$*

$Fe^{\cdot\cdot} \longrightarrow Fe^{\cdot\cdot\cdot} \quad + 0{\cdot}75$

$Hg_2^{\cdot\cdot} \longrightarrow 2Hg^{\cdot\cdot} \quad + 0{\cdot}92$

$Tl^{\cdot} \longrightarrow Tl^{\cdot\cdot\cdot} \quad + 1{\cdot}24$

$Co^{\cdot\cdot} \longrightarrow Co^{\cdot\cdot\cdot} \quad + 1{\cdot}8$

$Pb \longrightarrow Pb^{\cdot\cdot\cdot\cdot} \quad + 1{\cdot}8$*

PROBLEMS.

Electrical and Chemical Energy.

1. A cell containing concentrated aqueous HCl with chlorine and hydrogen electrodes, when allowed to work in a calorimeter absorbed 509 calories during the passage of 2 F.

The energy produced in the external circuit was equivalent to 22,509 calories. What is the chemical energy (change of intrinsic energy q) of the formation of 2 HCl under these conditions?

Dolezalek.

Answer $q = + 22{,}000$ calories.

2. A form of cell has been realised in which gravitational is converted into electrical energy. The poles consist of a long and a short column of mercury, of which the lower ends are separated from the electrolyte by a diaphragm which is permeable to the electrolyte, but impermeable to the metallic mercury. The current-giving process consists in the solution of mercury at the end of the long column, and the deposition of mercury at the shorter. The electrical energy will then be equal to the mechanical work which could have been obtained by the fall of the mercury through the difference in height.

Since the gravitational work does not vary with temperature, prove that the change in free energy A is equal to the change in total energy q.

What must be the difference in height between two columns of mercury at 0° ($D = 13{\cdot}6$), in order that the electromotive force of the cell may be 1 millivolt?

The variation in the gravity constant (981) with height is neglected.

The mercury is present in the solution as mercurous ions.

Answer $h = 3{\cdot}618$ metres.

The number of gram centimetres concerned with the transfer of 1 gram equivalent must be converted into joules and equated to 1 volt faraday expressed in joules.

3. The E. M. F. of the dilute Daniell cell at 0° C. is 1·0962 volts.

The heat of replacement of Cu by Zn (1 gram atom) in dilute $CuSO_4$ is 50,110 calories (decrease of chemical energy q). Find the heat absorbed or evolved by the cell during the passage of 2 F, and compare it with the reversible heat Q as deduced by the temperature co-efficient of E. M. F. $= + 0{\cdot}000034$ volt per degree.

Answer 416 calories absorbed.
428 ,, ,,

$$Q = EF - q, \text{ and } Q = FT\frac{dE}{dt}.$$

Jahn (*Wied. Ann.* 28, 21—43, etc.).

4. An accumulator containing H_2SO_4 of density 1·153 is found to have a temperature coefficient of $+ 0_3345$ at 0° C.

How much heat (in joules) is absorbed or evolved when 1 coulomb is taken from the cell?

Answer $Q = 0{\cdot}092$ joules absorbed.

What is the relation between the electrical work and the loss of chemical energy?

Answer The former is **104** per cent. of the latter.

5. Show that the association of a positive temperature coefficient with a positive latent heat ($+Q =$ heat absorbed) follows from the principle of mobile equilibrium (p. 96).

6. Irreversible heat is always generated in the cell by ohmic resistance and diffusional changes, when current passes. This increases the observed reversible heat Q when the latter is negative and decreases it when it is positive (according to the convention $+Q =$ heat absorbed).

Streintz measured the reversible heat of a lead accumulator by allowing it to work in a calorimeter at 0°. The charging and discharging current was 0·100 ampere. The heat developed in the calorimeter was 0·004 joule per second during discharge, 0·0228 during charge. Find the reversible heat of reaction per coulomb passing, and the temperature coefficient of electromotive force.

Answer $Q = \mathbf{0{\cdot}094}$ joule.

$$\frac{dE}{dt} = +\,\mathbf{0{\cdot}00034}.$$

The net heat effects (evolved) during the charge and discharge are $I^2R + QI$ and $I^2R - QI$.

The internal resistance of the cell is assumed to be constant. For a fuller account of the cause of the irreversible heat effect, see Problem 78, p. 274.

Dolezalek ("Lead Accumulator," p. 33).

7. When 48,270 coulombs were taken from a cell, the heat absorbed, corrected for resistance heating was found to be 1,153 calories, at 17° C.

Find $\frac{dE}{dt}$ in millivolts per degree.

Answer $+\,\mathbf{0{\cdot}345}$.

8. The E. M. F. of the combination:

$$Hg,\ HgCl \mid KCl \mid KNO_3 \mid KOH \mid Hg_2O \mid Hg$$

is 0·1483 volt at 18°·5; the temperature coefficient is $+ 8{\cdot}37 \times 10^{-4}$ volts per degree; what is the heat of the reaction:

$$HgCl + KOH = \tfrac{1}{2}\,Hg_2O + \tfrac{1}{2}\,H_2O + KCl$$

which occurs in the cell?

Answer — **2,205** calories.

Bugarsky (*Zeitsch. anorg. Chem.* (1897), 14, 145).

(See also Donnan and Allmand, *Journ. Chem. Soc.* (1911), 99, 845.)

9. The temperature coefficient of E. M. F. of an accumulator, containing 78 mols. of H_2O to 1 mol. of H_2SO_4 is zero. What is the electromotive force?

$$PbO_2 + H_2SO_4 \times 2\,H^{\cdot} + 2\,\ominus = PbSO_4 + 2\,H_2O$$

$$Pb + SO_4'' = PbSO_4 + (2\,\ominus).$$

One molecule of H_2SO_4 disappears for each faraday produced.

Answer $E = 1{\cdot}86$ volts.

(See Problems 8, 9, p. 24.)

Dolezalek ("Lead Accumulator").

10. An accumulator containing acid of density **1·15** ($H_2SO_4 + 21\ H_2O$) has a temperature coefficient $\dfrac{dE}{dt} = + 0{\cdot}4 \times 10^{-3}$, and an E. M. F. of 1·96 volts at 17° C.

Find the loss of chemical energy q, the latent heat Q and the loss of free energy A, when 1 coulomb is taken from the cell (neglecting the energy spent in overcoming the internal resistance of the cell).

$$\text{Answer}\quad \left.\begin{array}{l} q = \mathbf{1{\cdot}846} \\ Q = \mathbf{0{\cdot}116}\ \text{(absorbed)} \\ A = \mathbf{1{\cdot}96} \end{array}\right\}\ \text{all in joules.}$$

(See last Problem.)

Does the energy q appear as heat?

11. The E. M. F. of the Cd normal cell is 1·0184 at 18°, and the temperature coefficient $\frac{dE}{dt}$ is $-\ 0{\cdot}0_4350$ volt per degree. What is the heat of the total reaction for each gram atom of cadmium dissolved?

Answer **198,560** joules.

12. The reaction in the Clark cell:

$$Zn + \frac{7}{a-7}\ ZnSO_4\ a \cdot H_2O + Hg_2SO_4 = 2\ Hg + \frac{a}{a-7}$$

$(ZnSO_4 + 7\ H_2O)$ evolves 340,000 joules. What is the value of $\frac{dE}{dt}$ if $E = 1{\cdot}4291$ at 18° C.?

Answer $\frac{dE}{dt} = -\ \mathbf{0{\cdot}00114}$.

13. Consider two accumulators kept at 0° C., containing (1) 35·26 per cent. of H_2SO_4 (2) 64·5 per cent. of H_2SO_4.

The total reaction which occurs during discharge may be divided into two parts: (1) the withdrawal of H_2SO_4 and the addition of H_2O (evolving q_1, q_2 calories); (2) the chemical reaction symbolised in the equations of Problem 9, p. 25 (evolving q calories).

The heat evolution q is supposed to be the same in the two cells.

If the two cells are coupled in opposition (the peroxide plates being directly connected) the cell containing the stronger acid will discharge through the other, and the net E. M. F. of the combination may be found from the equations:

$$A_1 = q_1 + q + T\frac{dA_1}{dT}$$

$$A_2 = q_2 + q + T\frac{dA_2}{dT}.$$

The amounts of heat corresponding to the withdrawal and addition of H_2SO_4 and water may be calculated as in Problem 22, p. 32.

14. What is the net electromotive force of the above combination, assuming the latent heats of the cell reactions to be zero?

Answer $\Delta E = \mathbf{0{\cdot}304}$ volt.

15. Actually, the temperature coefficient of the weaker cell is $+ 0{\cdot}11$, and that of the stronger $+ 0{\cdot}04$ millivolt per degree. What is the corrected value of the electromotive force?

Answer $\Delta E = \mathbf{0{\cdot}284}$ volt.

Dolezalek ("Lead Accumulator").

16. The relation between the concentration of acid (in gram molecules per litre) and E of a Pb, PbO_2 cell is given by the simplified expression:

$E = 1{\cdot}92 + 0{\cdot}15 \log C$ (see Problem 77, p. 274).

The expression is valid for dilute acids ($<5N.$) at 18° C.

Hence, deduce a formula connecting $\frac{dE}{dt}$ millivolts (per degree), and C for acids so dilute that the heat of further dilution is *nil.*

Also, find the temperature coefficient $\frac{dE}{dt}$ for $N.$ and $\frac{N}{10}$ acid, at 18° C.

$$\text{Answer} \quad \frac{dE}{dt} = 0{\cdot}52 \log C + \text{constant},$$

$$\frac{dE}{dt} = +\mathbf{0{\cdot}15} \text{ and } -\mathbf{0{\cdot}37} \text{ millivolt.}$$

For $\frac{dE}{dt} = \frac{E}{T} - \frac{q}{23{,}073T}$ where q = heat for 1 F.

17. The concentration chain:

$$Pb \mid PbSO_4H_2SO_4(C_2) \mid H_2SO_4(C_1)PbSO_4 \mid Pb$$

is capable of furnishing current at the expense of the energy of dilution of the H_2SO_4—that is, the action is such that H_2SO_4 is formed in the weaker acid.

Write equations for the changes which will occur in each compartment if $C_2 > C_1$.

What would be the loss of H_2SO_4 in C_2 on the passage of $1F_1$ if all the current were carried by $H^{\cdot}$?

Answer—

(C_2) $Pb + SO''_4 = PbSO_4 + 2 \ominus$ in concentrated acid negative electrode.

(C_1) $PbSO_4 + 2 \ominus = Pb + SO''_4$ in dilute acid positive electrode.

One equivalent of H_2SO_4 would be lost in C_2 during the passage of $1F$.

Dolezalek (" Lead Accumulator ").

18. A cell constructed as above contained 1 litre of 0·2 per cent. H_2SO_4 in C_1 and 1 litre of 1·35 per cent. H_2SO_4 in C_2 (by weight). What will be the concentration in each compartment when a current of 1 ampere has been taken out of the cell for one hour?

The changes in concentration are modified by ionic migration across the central partition. The transport number of $H^{\cdot}$ in H_2SO_4 is 0·8 (see p. 178).

Answer In C_1 **0·345**, in C_2 **1·21** per cent. of H_2SO_4.

1 mol. of H_2SO_4 is formed in C_1 for each $2\,F$ passing.

$1 - \nu_K$ mols. of SO''_4 passes out of C_1,

$2\,\nu_K$ mols. of $H^{\cdot}$ passes into C_1;

$\therefore$ the net H_2SO_4 formed in C_1 is $1 - (1 - \nu_K) = \nu_K$.

In C_2 1 mol. of SO_4 is used up, $1 - \nu_K$ mols. enter;

$\therefore$ the net loss is ν_K.

Consequently, when $2\,F$ of current pass, C_2 loses ν_K of H_2SO_4 and C_1 gains the same

$$\frac{3{,}600 \times \cdot 8 \times 98}{96{,}540 \times 2} = 1\cdot 45 \text{ grams of } H_2SO_4$$

$$\cdot 2 + 1\cdot 45 = 1\cdot 65, \text{ etc.}$$

19. The principle that the current flows in such a direction as to dilute the stronger solution may be applied to the combination:

$$PbO_2 \mid PbSO_4\ H_2SO_4(C_2) \mid H_2SO_4(C_1)PbSO_4 \mid PbO_2$$

Show that the current flows in the opposite direction to that of the last combination, Problem 17, and write equations for the reaction which occurs.

The numerical values of the acid concentration and quantity being the same as before, find the composition of the stronger solution C_2 when 1 ampere hour is taken out of the cell.

Answer $PbO_2 + H_2SO_4 + 2\,H^{\cdot} + 2\,\ominus = PbSO_4 + 2\,H_2O.$

Thus, the electrode in the concentrated solution assumes a positive charge (compare the behaviour of the $Pb\ PbSO_4$ cell), and consequently the H ions migrate into C_2. $2\,\nu_K$ gram ions of H enter, 1 of SO_4 is used up; $1 - \nu_K$ of SO_4 migrates out, and 2 of H_2O are formed, when 2 F of current pass.

$$\text{In } C_2 \left\{ \begin{array}{ll} \text{Loss of } H_2SO_4 & = (2 - \nu_K) \text{ mols.} \\ \text{Gain of } H_2O & = 2 \text{ mols.} \end{array} \right\} \text{ for } 2\,F$$

$$\frac{3600}{96540 \times 2} = 0{\cdot}01865.$$

Answer. The final composition of the stronger solution is 11·3 grams of H_2SO_4 to 958·8 grams of H_2O.

Electromotive Force and Concentration.

20. The following values of $\frac{RT}{F} \times 2{\cdot}303$ have been calculated at the absolute temperatures corresponding to the Centigrade temperatures of the first column. For the value of $\frac{R}{F}$, see Problem 12, p. 17.

$t°$ C.	$\frac{RT}{F} \times 2{\cdot}303$	$t°$ C.	$\frac{RT}{F} \times 2{\cdot}303$
0°	0·05418	17°	0·05754
15°	0·05715	18	0·05775
16	0·05735	25	0·05913

A concentration cell is made up with silver electrodes immersed in decinormal and centinormal silver nitrate solutions.

What is the electromotive force of the cell at 20°, ignoring the diffusion E. M. F. at the contact of the two solutions, and using the equation (2), p. 234?

Answer $E = 0{\cdot}116$ volt.

For $$E = \frac{NRT}{n_K F} \log \frac{10}{1}.$$

Each mol. of $AgNO_3$ is completely dissociated, giving two molecules effective in producing osmotic pressure (see Introduction, p. 233). Therefore $E = 2 \times 0{\cdot}058$.

(See Table above, p. 245.)

21. What is the electromotive force at 18° of the cell described above when the ionic migration across the surface of separation of the $AgNO_3$ solutions is taken into account? (See equations (4) or (10), pp. 234, 235.)

The value of $\frac{R}{F}\log$ is taken as 0·0002 in round numbers, and the transport number v_A of the anion in $AgNO_3$ is 0·527.

Answer $E = 0{\cdot}061$ volt.

22. According to a theory developed by Nernst, the osmotic work obtainable from a cell of this kind depends rather upon the ionic than upon the total salt concentrations.

The degree of dissociation of the decinormal silver nitrate is 0·872; that of the centinormal may be taken as 1·0.

What difference will this correction make in the calculated E. M. F.?

Answer $$E = \frac{RT}{n_K} \cdot 2\ v_A \log \frac{a_1 C_1}{a_2 C_2}$$
$$= 0{\cdot}0576 \text{ volt.}$$

23. Of what magnitude and in what direction is the diffusion potential at the surface of contact between 0·01 normal and 0·001 normal HCl at 18°? Assume complete dissociation and use equation (8), p. 235 (see Table, p. 245).

If $\frac{U_A}{n_A} > \frac{U_K}{n_K}$ the weaker solution a_2C_2 will be positive.

Answer $E = 0{\cdot}038$ volt.

(See Diagram below.)

24. From the mean ionic conductivities l_A and l_K of $Ag^{\cdot}$ and NO'_3 between the concentrations 0·005 and 0·10 normal (see Table, p. 179), calculate the sign and magnitude of the diffusion E. M. F. at the junction of the two solutions.

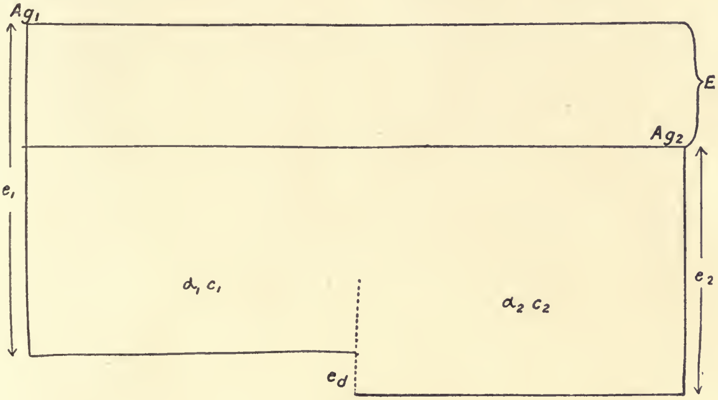


Fig. 12.

For the concentrations C_1 and C_2 of equation (3), p. 234, substitute the ionic concentrations a_1C_2 and a_2C_2.

Answer $E = 0{\cdot}0046$ volt.

The weaker solution is negative.

25. An electrode reversible with respect to hydrogen ions may be made by passing H_2 gas over the surface of a palladium or platinised platinum electrode, dipping in acid. Such an electrode is analogous in its action to the Ag electrode already considered, provided that the hydrogen solution pressure (see p. 252) is the same at the two electrodes.

What would be the E. M. F. of a 0·1, 0·01 normal HCl

H_2Pt cell, the former acid being dissociated to 91 and the latter to 96 per cent. (Smale) at 15° . $v_A = 0{\cdot}172$?

The two halves are connected (1) by a 0·01 normal solution of HCl; (2) by a concentrated solution of ammonium nitrate, which eliminates the diffusion E. M. F.

Abegg and Cumming (Trans. Far. Soc. (1906—1907), 2, 213).

Answer $E =$ **0·019** volt.
$=$ **0·056** „

(See equation (4).)

26. The combination:

$Hg \mid HgCl$ (solid) 0·1 $HCl \mid$ 0·01 HCl $HgCl$ (solid) $\mid Hg$

is reversible with respect to chlorine ions. When a current is taken from the cell Hg is ionised and forms solid $HgCl$ in one half. In the other half Hg is deposited from solid $HgCl$. The reactions take place in such a way as to equalise the concentrations of HCl.

The sign of the electrodes depends on the $Hg^{\cdot}$ concentration as before, but this must now be regarded as connected with the variable Cl' concentration by means of the solubility product (see p. 181), since $[Hg^{\cdot}] \times [Cl'] = K[HgCl]$.

The $[Hg^{\cdot}]$ will now be highest in that half in which the $[Cl']$ is the lowest.

What is the theoretical E. M. F. of such a concentration chain with diffusion, and what would be the E. M. F. observed if the diffusion E. M. F. were eliminated (18°).

The ionic conductivities l_A and l_K of $[H^{\cdot}]$ and $[Cl']$ may be taken as the means of l_{K_1} and l_{K_2}, and of l_{A_1} and l_{A_2} at the two concentrations C_1 and C_2.

Answer $E =$ **0·096** (with diffusion).
$=$ **0·057** (without diffusion).

27. What is the E. M. F., taking into account the different degrees of dissociation, of the HCl as given in the last problem?

Answer $E =$ **0·094**.

28. What is the E. M. F. of the mercury-calomel concentration chain as above if KCl of the concentrations $C_1 = 0{\cdot}125$ and $C_2 = 0{\cdot}0125$ is substituted for the HCl (18°)?

(v_K of K in $KCl = 0{\cdot}49$).

Answer $E = 0{\cdot}057$.

29. What is the calculated E. M. F. of a cell consisting of hydrogen electrodes in 0·01 and 0·001 normal acetic acid at 17° (without diffusion potential), the ionic conductivities being $l_A = 31{\cdot}5$, $l_K = 312$; K for $HA = 1{\cdot}8 \times 10^{-5}$ (see Problem 24, p. 190 and p. 246)?

Answer $E = 0{\cdot}0055$ volt.

30. The diffusion E. M. F. at the surface of separation of two binary electrolytes of the same total concentration, with ionic conductivities l_K, l_A ; l'_K, l'_A is given by Planck's formula:

$$e_d = \frac{RT}{nF} \log \frac{l_K + l'_A}{l'_K + l_A}.$$

From the following values of l_A, etc., calculate e_d for the combinations:

$HCl \mid KCl$; $HCl \mid NaCl$; $KCl \mid NaCl$.

$K = 52 \quad Na = 32 \quad H = 272 \quad Cl = 54.$

Answer $e_d = 0{\cdot}0282, 0{\cdot}0334, 0{\cdot}0052$ volt.

31. A cell is made up with electrodes of amalgams containing different concentrations C_1, C_2 of the same metal, dissolved in Hg. The electrolyte is a salt of the dissolved metal. Find an expression for the maximum osmotic work obtainable, when one equivalent of the metal is transported from C_1 to C_2.

Answer $\dfrac{RT}{n} \log \dfrac{C_1}{C_2}$.

If the value of R in joules is 8·287, find the molecular weight (M) of Cu and Na in their amalgams from the following:

Cu	t	C_1	C_2	E
17·3	17·3	$0{\cdot}0_{3}3874$	$0{\cdot}0_{4}9587$	0·01815
20·8	20·8	$0{\cdot}0_{3}4472$	$0{\cdot}0_{3}16645$	0·0124
Na	20·2	$0{\cdot}0_{3}3325$	$0{\cdot}0_{4}953$	0·0327

The electrolytes were solutions of cupric and sodium salts.

Answer $M =$ **63·3** and **63·7** (Cu)
$=$ **22·2** (Na).

$$\text{Note that } \frac{1}{n} = \frac{\frac{M}{n}}{M} = \frac{\text{Equivalent weight}}{M}.$$

32. The maximum work of gas reactions varies according to the arbitrary partial pressures of the reactants and resultants before and after the reaction.

(See p. 142.)

So, also, if the combination can be effected reversibly by means of a gas cell, the maximum work, and therefore the electromotive force varies with the partial pressures of the reacting gases at the electrodes.

A reversible chlorine electrode can be made by saturating platinised platinum with chlorine at atmospheric pressure.

A cell (1) containing a hydrogen electrode and a chlorine electrode of this type with the gases at a pressure of 1 atmosphere is set in opposition to a similar cell (2), in which the hydrogen and chlorine are each mixed with 50 per cent. by volume of an indifferent gas.

How much of each gas will pass from the lower to the higher pressure when 1 F is taken from the combination?

If the hydrochloric acid concentration is the same in each cell, determine the direction of the current and the magnitude of the electromotive force.

Answer Positive current will flow from H_2 (2) to H_2 (1) in the outside circuit. $E =$ **0·0175** volt.

33. The following experimental results will serve to illustrate the method of determining hydrogen ion concentration from E. M. F. data.

A wire was calibrated by the method of Strouhal and Barus (see Ostwald, Luther, *Phys. Chem. Messungen*), and the following readings corresponded to 0·1, 0·2, etc., of its total resistance: 9·83, 19·91, 30·05, 40·13, 50·23, 60·31, 70·38, 80·39, 90·43, 100·00 centimetres.

The ends of the wire were connected with the poles of a single lead accumulator (B), and the fall of potential along the wire determined in the usual manner with a cadmium standard cell (Cd).

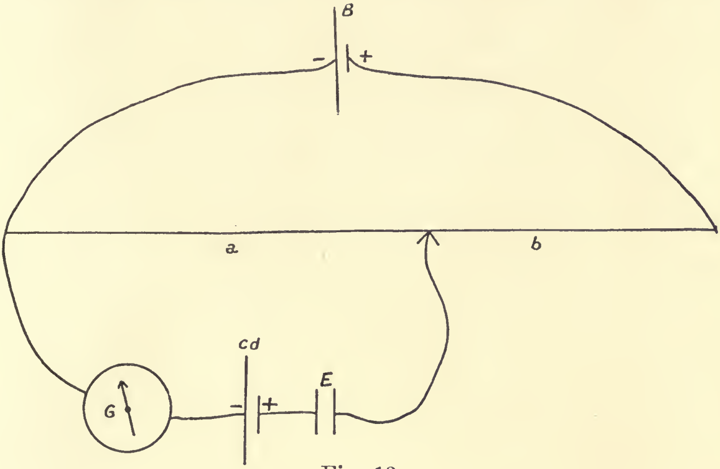


Fig. 13.

The E. M. F. of the cadmium standard cell was 1·019 at 16°·0, which was balanced by 50·65 centimetres of the wire which carried the current.

A combination of: (E on Diagram)

H_2Pt | 0·01 HCl | eliminator of potential (e_d) | 0·1 Na_2HPO_4 | H_2 Pt

was connected successively to the positive and negative poles of the standard cell as shown.

The corresponding readings on the wire were 31·00 and 70·24 centimetres, while the combination without the cadmium cell balanced at 19·35 centimetres.

Calculate E of the H_2Pt combination to 3 places of decimals, and the hydrogen ion concentration of the phosphate solution, if that of the HCl is 1×10^{-2}.

Answer $E = 0·393$ volt.

$[H^{\cdot}] = 1·48 \times 10^{-9}$.

34. What is the electromotive force between two hydrogen electrodes immersed in dilute HCl, and saturated at pressures of 1·0 and 0·5 atmosphere ?

Answer $E = 0·0087$ volt.

35. The hydrogen ion concentration of physiological fluids may be determined by the hydrogen electrode method (See Höber, "Chemie der Zelle.")

Blood serum is naturally in equilibrium with CO_2 having a partial pressure of about 0·05 atmosphere. The hydrogen used to saturate the electrode should therefore contain the corresponding percentage of CO_2, if the solution equilibrium is not to be disturbed.

The observed E. M. F. must be reduced to that which would be obtained if pure H_2 were used. This can be done by a deduction of the work required to reduce the partial pressure of H_2 from 1·0 to 0·95 atmosphere.

Höber has proved experimentally that the E. M. F. of H_2 electrodes can be calculated in this way from $RT \log p$ down to a partial pressure of hydrogen = 0·2 atmosphere (0·8 atmosphere CO_2).

Two half cells were connected by an eliminator of diffusion E. M. F. One half contained a hydrogen electrode saturated with H_2 containing 6 per cent. of CO_2 in serum of unknown acidity. The other half contained a hydrogen electrode saturated with H_2 at atmospheric pressure in a solution of $[H^{\cdot}] = 1 \times 10^{-7}$.

What is the hydrogen ion concentration of the serum, if the E. M. F. of the combination is 0·0074 volt (serum negative)?

Answer $[H^{\cdot}] = 7·1 \times 10^{-8}$.

Since the serum electrode is negative, gaseous hydrogen is, in that half, converted into hydrogen ions. The maximum work of the reaction would therefore be greater if the partial pressure of the hydrogen were greater in the serum half of the combination.

36. Two hydrogen, chlorine cells are made up according to the following specifications.

The electrodes are of platinum saturated with pure hydrogen and chlorine, each at a total pressure of 1 atmosphere. (See Problem 25, p. 247.)

The electrolyte in cell (1) is 11·62 *N.* HCl, that in cell (2) 5 *N.* HCl.

The partial pressures of hydrochloric acid gas over aqueous acids of these concentrations has been found to be 18·9 and 0·2 millimetres, respectively.

The cells are connected in opposition to one another at 30° C.

Prove that the electromotive force of the combination can be calculated from a combined knowledge of the vapour pressures of HCl and of the partial pressures of the electrode gases.

What is the numerical value of the total net electromotive force, and of the parts into which it may be divided? The parts are the maximum work due to the expansion of the HCl gas, and that due to the expansion of the electrode gases.

If b is the barometic pressure, an equation will be obtained of the form:

$$E = \frac{RT}{nF}\left(\log\frac{p_1}{p_2} + \log\frac{b - p_1}{b - p_2}\right).$$

Answer E (total) $= 0·181$ volt.
E_1 (HCl gas) $= 0·174$,,
E_2 (H_2 and Cl_2) $= 0·007$,,

Dolezalek (*Zeitsch. physikal Chem.* (1898), 26, 33).

Single Potential and Decomposition Voltage.

37. The E. M. F. of the combination:

$$H_2Pt \mid N.HCl \mid N.HCl \mid HgClHg$$

was found to be 0·289. The single potential of the normal HCl calomel electrode is 0·001 volt less than that of the normal KCl calomel electrode. If the degree of dissociation of HCl is 0·78, find the potential of the calomel electrode against a normal ionic hydrogen electrode taken as 0.

Answer + **0·284** volt.

$$e_H = e_o - \frac{RT}{nF} \log [H^{\cdot}].$$

$$E_{(\text{obs.})} = e_c - e_H. \qquad e_o = 0.$$

$$\therefore E_{(\text{obs.})} = e_c + \frac{RT}{nF} \log [H^{\cdot}].$$

Wilsmore (*Zeitsch. physikal Chem.*, 35, 302).

38. Prove, by reference to the Table (p. 237), and otherwise, that the higher the positive potential of a kation, the greater is its tendency to come out of solution, and the higher the positive potential of an anion the greater its tendency to go into solution.

The evidence of the dropping electrode tends to prove that the absolute single potential of the normal KCl calomel electrode is + 0·56 volt (electrode positive) (Ostwald, Paschen).

Palmaer (*Zeitsch. Physikal Chem.* (1899), 28, 259).
(*Zeitsch. Elektrochem.* (1903), 9, 754).

From the data of the last problem, find the absolute potential of the normal hydrogen electrode against its solution.

Answer + **0·277** volt.

Draw a diagram (similar to that in Problem, p. 247), illustrating these steps of potential.

39. Draw a diagram to scale, illustrating the effects of ten-fold dilution on the single potentials of copper and zinc in solutions of their respective ions.

(See Table, p. 237, and equation (14), p. 236.)

40. What is the theoretical E. M. F. (ignoring diffusion potential) of a Daniell cell containing $ZnSO_4$ and $CuSO_4$, normal with respect to $Zn^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$?

The copper solution is diluted until it is 0·01 normal with respect to $Cu^{\cdot\cdot}$, the $ZnSO_4$ solution until it is 0·1 normal with respect to Zn. What is the new E. M. F. at 18°?

Answer $E =$ **1·100** and **1·071**.

Show that the change of E. M. F. would be the same, if the $ZnSO_4$ alone were diluted to the extent mentioned above.

41. If $ZnSO_4$ is 11·4 per cent. dissociated in normal solution, what is the single potential of Zn against this solution?

Hence $E = -$ **0·79** Answer.

Foerster ("Elektrochemie Wässriger Lösungen").

42. What must be the concentration of Br', in order that Cl_2 should be liberated alone at the anode from a well-stirred mixture of aqueous HBr and HCl, containing the latter acid in decinormal ionic concentration?

Note the convention with regard to the sign of the anion potentials (equation (14), p. 237).

Answer $C_{Br} = \mathbf{2 \times 10^{-6}}$

$$e_{Cl} = 1{\cdot}35 + \frac{0{\cdot}058}{-1} \log C.$$

What is the difference between the potential required to separate Cu, and that required to separate Ag from: (1) A decinormal, (2) a centinormal solution of the two ions at 18°?

Answer The Cu requires a higher E. M. F. by **0·431** volt, in the first, and **0·402** volt, in the second case.

43. The electromotive force of a concentration chain:

$$Zn \mid ZnBr_2 \mid AgBr \mid Ag$$

was found to be + 0·839 volt (without diffusion potential).

The concentration of the $ZnBr_2$ was four equivalents to the litre; the degree of dissociation 10·5 per cent.

The concentration of the bromine ions in the silver half was $5{\cdot}3 \times 10^{-3}$.

What is the difference between the normal potentials of Ag and Zn?

Answer **1·536** volts.

Measurements of Jahn, Wright, Thompson. See Wilsmore (*loc. cit.*, p. 254).

44. The cell:

$$Ag \mid 0{\cdot}1\ N.AgNO_3 \mid 1{\cdot}0\ N.KCl \mid AgClAg$$

has an electromotive force of 0·52 volt (without diffusion E. M. F.) at 18°.

Assuming complete dissociation of the $AgNO_3$ and KCl, find the solubility of $AgCl$ in mols. per litre.

Answer $C_{AgCl} = \mathbf{1{\cdot}1 \times 10^{-5}}$.

After the concentration of the silver ions has been obtained from the electrometric data, the value of $[Ag.] = [AgCl]$ can be deduced from the solubility product.

(See Problem, p. 221.)

45. Taking the electrode potential e_o of $Cu \longrightarrow Cu^{\cdot\cdot}$ as 0 33 ($e_H = 0$) and the absolute potential of the calomel electrode as 0·56, how many kilowatt hours are gained at the kathode of a plating bath during the deposition of 31·8 grams of copper?

Answer **0·016**.

Find the absolute potential of the copper, against the solution, and from this the work done (in joules) by the deposition of one equivalent.

"Copper," Donnan ("Handbuch, Abegg").

46. According to Labendzinski the difference of potential between copper and a normal solution of its ions is 0·58 volt;

the temperature coefficient of the E. M. F. is $0{\cdot}0_3756$ (hot solution positive).

What are the changes of chemical and free energy when 1 gram atom of Cu is precipitated from such a solution at 18°?

Answer $A =$ **26,800** calories.
$q = A - Q =$ **16,600** calories.

(See equation (1), p. 233.)

47. The decomposition potential of a given solution may often be calculated from the normal potentials of Table, p. 237, and the law of logarithmic concentrations.

If the convention as to signs (p. 236) is adopted together with a further convention to the effect that the decomposition potential shall be positive if work has to be done in order to electrolyse the solution, then it follows directly from equations that:

$$E_d = e_A - e_K = e_{OA} - e_{OK} + \frac{RT}{n_A F} \log C_A - \frac{RT}{n_K F} \log C_K.$$

Thus, the decomposition potential of a saturated solution of $AgCl$ may be obtained from the normal potentials and the solubility result of Problem 44, p. 256.

$$E = 1{\cdot}35 - 0{\cdot}80 - 2 \times 0{\cdot}058 \times \log (1 \times 10^{-5}).$$
$$= \mathbf{1{\cdot}13} \text{ volts. Answer.}$$

Note again the rule as to the negative sign of $n_A F$.

48. The decomposition potentials of solutions of HgI_2 and PbI_2 saturated at 18° are $+\ 0{\cdot}53$ and $+\ 0{\cdot}86$ volt respectively.

Find the solubilities.

Answer HgI_2 **1×10^{-10}** gram equivalents per litre.
PbI_2 **5×10^{-3}** ,, ,, ,, ,,

$$0{\cdot}53 = 0{\cdot}54 - 0{\cdot}86 - 0{\cdot}087 \log C.$$
$$0{\cdot}86 = 0{\cdot}54 - (-\ 0{\cdot}12) - 0{\cdot}08 \log C.$$

Bodländer (*Zeitsch. physikal Chem.* (1898), 27, 55).

49. A voltage in excess of the theoretical is required to liberate hydrogen from many metals. This excess voltage

ϵ increases with current density, and varies for different metals. Therefore, from equation (14), p. 236,

$$e_H = -\epsilon + e_o + 0{\cdot}058 \log C_H.$$

Thus, if the over-voltage of H_2 on Zn is 0·70, the hydrogen will be evolved from a solution normal with respect to the $H^{\cdot}$, and 0·114 normal with respect to $Zn^{\cdot\cdot}$ (2 N. $ZnSO_4$), at a potential about 0·1 volt lower than that required to deposit Zn.

Thus $e_H = -0{\cdot}70 + 0{\cdot}277 + 0{\cdot}058 \log 1 = -$ **0·423.**

$eZn = -0{\cdot}493 + 0{\cdot}029 \log 0{\cdot}114 = -$ **0·520.**

(See Foerster ("Elektrochemie Wässriger Lösungen").)
Caspari. (*Zeitsch. Elektrochem.* (1900), 7, 111).
Tafel (*Zeitsch. physikal Chem.* (1905), 50, 641).

50. The over-voltage ϵ for hydrogen on nickel at a current density of 0·1 ampere is 0·74 volt in a double normal solution of H_2SO_4 ($[H^{\cdot}] = 1$); what is the value in volts of the difference between the E. M. F. required to deposit Ni and that required to evolve H_2 from a solution normal with respect to Ni ($a = 11$ per cent.), and double normal with respect to H_2SO_4?

Answer The tendency to deposit Ni is greater by **0·484** volt.

Take e_o for $H = +0{\cdot}277$, and e_o for $Ni = +0{\cdot}049$ (calomel $= +0{\cdot}56$).

51. The combination:

$$HgHgCl \mid N.KCl \mid N.NaOH \mid HgOHg$$

has an electromotive force of 0·1541 volt at 25° C. (calomel positive).

The chemical reaction which furnishes the electrical energy is:

$$HgCl + NaOH = HgOH + NaCl.$$

The single potential e_o of the calomel half is $+0{\cdot}2873$ volt.

The ionic conductivities are:

$$l(Na) = 51{\cdot}0 \qquad l(Cl) = 74{\cdot}3$$
$$l(K) = 74{\cdot}5 \qquad l(OH) = 195{\cdot}9$$

Find the single potential of the alkaline half.

Answer **0·1135** volt (*Hg* positive to solution).

The problem requires a knowledge of the diffusion potential e_d.

The Planck formula (Problem 30, p. 249), and the velocities of the two anions and kations u_{K_1}, u_{A_1}; u_{K_2} u_{A_2} (or the ionic conductivities l_K etc.) being given, show by a diagram or otherwise that solution (2) will be positive to solution (1) when $u_{K_1} + u_{A_2} > u_{K_2} + u_{A_1}$.

Donnan and Allmand (*Journ. Chem. Soc.* (1911), 99 and 100, 850).

52. The concentration of an ion-forming gas X_m in a solution surrounding an electrode, is, according to the laws of chemical equilibrium connected with the concentration of its ions X'_n by an equation of the form:

$$[X_m]^n \rightleftarrows K[X'_n]^m$$

The single potential of the electrode formed of such a gas is given by the equation:

$$e = \frac{RT}{n'F} \log \frac{[X_m]^n K}{[X_n]^m},$$

n' referring to the valency of the ion.

The normal potential e_o is, as before, numerically equal to the single potential when $[X_m]$ and $[X_n]$ are both equal to 1.

$$e_o = \frac{RT}{n'F} \log K.$$

Apply these results to the following measurements of the potential of a normal *KCl* calomel electrode against a chlorine electrode in hydrochloric acid.

The concentration of chlorine in the solution was determined by titration with KI and a one hundredth molecular normal solution of $Na_2S_2O_3$. The solution was half normal with respect to HCl which was taken as 87 per cent dissociated.

Number of c.c. of thiosulphate equivalent to 10 c.c. of electrode solution.	Positive potential against calomel electrode.
2·07	0·949
91·20	0·997

$$t = 17^\circ \text{ C.} \quad \frac{R}{F} \log = 0{\cdot}0002.$$

Sullivan (*Zeitsch. physikal Chem.* (1899), 28, 38.

What is the absolute normal positive potential e_o of the chlorine electrode above its solution, if the corresponding absolute potential of the calomel electrode is taken as $+ 0{\cdot}56$ volt?

Answer $e_o = + 1{\cdot}566$ volts.

53. What will be the single potential e of a chlorine electrode, saturated at atmospheric pressure ($[Cl_2] = 0{\cdot}064$ mol. per litre), in a solution containing the same concentration of Cl' as before?

Answer $e = + 1{\cdot}601$ volts.

54. The electromotive force of the combination:

$$CuCu_2O \mid NaOH \mid H_2Pt$$

is 0·469 volt. The solubility product $H^{\cdot} \times OH'$ (K_w) in water and aqueous solutions is $0{\cdot}56 \times 10^{-14}$, and the single potential e_o of Cu against a normal solution of $Cu^{\cdot}$ ions is 0·454 volt (Bodländer und Storbeck).

Taking e_o for $H_2 \longrightarrow 2\, H^{\cdot}$ as 0, what is the value of the solubility product:

$$K[CuOH] = [Cu^{\cdot}] \times [OH'] ?$$

First, calculate the separate single potentials of $Cu^{\cdot} \longrightarrow Cu$ and $H^{\cdot} \longrightarrow H$ in terms of e_o.

The ionic concentrations $Cu^{\cdot}$ and $H^{\cdot}$ may be expressed as the quotient $\frac{K[CuOH]}{OH'}$.

The OH' concentration is, of course, common to the two equations.

$$e\,(Cu^{\cdot} \longrightarrow Cu) = e_o\,(Cu^{\cdot} \longrightarrow Cu) + 0{\cdot}058 \log [Cu^{\cdot}]$$

$$e\,(H^{\cdot} \longrightarrow H) = e_o\,(H^{\cdot} \longrightarrow H) + 0{\cdot}058 \log [H^{\cdot}]$$

$$Cu^{\cdot} = \frac{K[CuOH]}{[OH']} \qquad H^{\cdot} = \frac{K_w}{[OH']}$$

$$e\,(Cu^{\cdot} \longrightarrow Cu) - e\,(H^{\cdot} \longrightarrow H)$$

$$= 0{\cdot}454 - 0 + 0{\cdot}058 \log \frac{K[CuOH]}{K_w}$$

$$0{\cdot}469 = 0{\cdot}454 + 0{\cdot}058 \log \frac{K[CuOH]}{0{\cdot}56 \times 10^{-14}}$$

Answer $K[CuOH] = 1{\cdot}0 \times 10^{-14}$.

Allmand (*Journ. Chem. Soc.* (1909), 95, 2166).

55. In the cell:

$$Pt \left| \begin{array}{l} Cu\,(OH)_2 \\ Cu_2O \end{array} \right| NaOH \,\Big|\, H_2Pt$$

the reaction occurring is:

$$2\,Cu\,(OH)_2 \longrightarrow Cu_2O + 3\,H_2O.$$

Show how this can be expressed by the charging and discharging of ions at the electrodes.

The observed E. M. F. of the whole cell = 0·738 volt (PtH_2 negative), and $e_o\ (Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}) = 0{\cdot}204$ volts.

From this, combined with K_w and $K[CuOH]$, as found in the last problem, calculate the value of $K[Cu(OH)_2] = [Cu^{\cdot\cdot}] \times [OH']^2$.

Answer $K_i = \mathbf{1{\cdot}0 \times 10^{-19}}$.

The following are the reactions in the cell :

$$\begin{array}{lrcl}
\text{At kathode} & Cu^{\cdot\cdot} & \longrightarrow & Cu^{\cdot} + \oplus \\
 & Cu^{\cdot} + OH' & \longrightarrow & \tfrac{1}{2}\,(Cu_2O + H_2O)\ \text{solid.} \\
 & Cu\,(OH_2) & \longrightarrow & Cu^{\cdot\cdot} + 2\ OH'. \\
\text{At anode} & \tfrac{1}{2}\,H_2 + \oplus & \longrightarrow & H^{\cdot} \\
 & H^{\cdot} + OH' & \longrightarrow & H_2O. \\
\text{Total} & 2\ Cu\,(OH)_2 + H_2 & \longrightarrow & Cu_2O + 3\ H_2O.
\end{array}$$

By writing the equations of single potentials as in the last problem $e\ (Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}) = e_o\ (Cu^{\cdot\cdot} \longrightarrow Cu)$, etc., and subtracting, obtain an equation from which to calculate the value of $K[Cu(OH)_2]$.

The equilibrium constant of cuprous and cupric ions $\dfrac{[Cu^{\cdot\cdot}]^2}{[Cu^{\cdot\cdot}]} = K$ has been found by Bodländer and Storbeck to be $0{\cdot}5 \times 10^{-4}$.

The product $[Cu^{\cdot}] \times [OH]$ in a saturated solution of cuprous hydroxide has already been found (K_o).

Prove that the product $[Cu^{\cdot}] \times [OH]$ in a saturated solution of cupric hydroxide is equal to $\sqrt{K_i\,K}$, K_i being the solubility product of cupric hydroxide.

Allmand (*loc. cit.*).

56. Show how this accounts for the fact that a mixture of $Cu(OH)_2$ and finely divided Cu, when shaken in an alkaline solution, is completely reduced to Cu_2O. That the change must take place completely in one or the other direction could be predicted from the incompatibility of condensed systems.

What are the solubilities of cuprous and cupric hydroxides at 17° in gram molecules per litre ?

Answer $0{\cdot}5 \times 10^{-7}$ and 3×10^{-7}.

57. When iodine is dissolved in a solution of KI, there is a formation of complexes $(KI)_m\ (I_2)_n$.

Of these possible molecules, KI_3 exists almost exclusively in solutions of the KI and I_2 concentration considered.

For a demonstration of this and references to other papers on the question, see Laurie (*loc. cit.* below).

The reactions in solution are regulated by the equations:

$$KI \rightleftarrows K^{\cdot} + I'$$
$$KI_3 \rightleftarrows K^{\cdot} + (I_3)'$$
$$I'_3 \rightleftarrows I_2 + I'.$$

Two solutions, b and a are made up to contain I_2 and I' in the concentrations $[I_2]_b$ $[I']_b$ $[I_2]_a$ $[I']_a$, and a platinum electrode is immersed in each. When a current is allowed to pass, therefore, the reaction occurring is $I_2 \longrightarrow 2\,I'$ in the one cell and the reverse in the other.

The maximum work for the whole reaction can be calculated as before from the E. M. F., *i.e.*,

$$E = 0{\cdot}02955 \left(\log \frac{[I_2]_b}{[I']^2_b} - \log \frac{[I_2]_a}{[I']^2_a}\right) \quad . \quad (1)$$

The concentrations of the molecules and ions may be calculated as follows:

$$\frac{[KI] \times [I_2]}{[KI_3]} = K = \frac{[I_2] \times [I']}{[I'_3]} \quad . \quad (2)$$

if the degrees of dissociation of the KI_3 and KI are the same.

The following concentrations:

$C_1 =$ total KI $\qquad C_2 =$ total I_2 (as KI_3 and I_2)

can easily be determined analytically. The concentration of molecular I_2 in a saturated solution is taken as constant and equal to 0·00134 mol. per litre, which is the solubility in pure water. In unsaturated solutions let:

$$[I_2] = x;$$

then $$\frac{(a - b + x)\,x}{b - x} = k = 0{\cdot}00138 \text{ at } 25^\circ$$

Jakowkin (*Zeitsch. physikal Chem.* (1896), 20, 36).

$$\therefore x = \frac{KC_2}{C_1 - C_2 + K} \quad . \quad (3)$$

The two solutions have the compositions:

(*a*) Normal with respect to KI and 0·0005 N with respect to I_2.

(*b*) Normal with respect to KI and saturated with solid I_2.

By means of the value stated above for the constant K and the degree of dissociation (0·593) of the normal KI, calculate the iodine ion concentration of the solution "*b*," the E. M. F. (corrected for diffusion potential) being 0·118.

Laurie (*Zeitsch. physikal Chem.* (1909), 67, 627).

Answer $[I'] = 0{\cdot}264$.

First find $[I_2]$ from equation (3), introduce the value into equation (1), and solve.

58. The E. M. F. of the combination

$$\begin{array}{c|l|l|c} Ag & 1{\cdot}0\ NH_3 & 0{\cdot}0093\ AgNO_3 & Ag \\ & 0{\cdot}025\ AgNO_3 & & \end{array}$$

is 0·3879 volt, at 18°. What is the approximate concentration of silver ions in the ammoniacal solution, ignoring the diffusion potential, and assuming complete dissociation of the $AgNO_3$ on the right hand side?

Answer $[Ag^{\cdot}] = 1{\cdot}9 \times 10^{-9}$.

(See Problem 90, p. 225.)

59. In the problem referred to above it was proved that $KaC_s = [Ag]^m\,[NH_3]^{m+1}$. C_s is the total concentration, and a the degree of dissociation of the complex salt $(AgCl)_m\,(NH_3)_{m+1}$.

Determine the values of $\dfrac{m+1}{m}$ and of m, from the electromotive force of combinations (1) and (2) below:

$$(1)\quad \begin{array}{c|l|l|c} Ag & 0{\cdot}0034\ AgCl & 0{\cdot}0034\ AgCl & Ag \\ & 1{\cdot}0\ NH_3 & 0{\cdot}1\ NH_3 & \end{array}$$

$$E = 0{\cdot}1213 \text{ volt at } 18^\circ$$

$$(2)\quad \begin{array}{c|l|l|c} Ag & 0{\cdot}0379\ AgCl & 0{\cdot}000379\ AgCl & Ag \\ & 1{\cdot}0\ NH_3 & 1{\cdot}0\ NH_3 & \end{array}$$

$$E = 0{\cdot}1120 \text{ volt at } 19^\circ{\cdot}5.$$

Answer $\frac{m+1}{m} = 1{\cdot}98 \quad \therefore m = 1$ from . (1)

$m = 0{\cdot}97$ from . . . (2)

(1) The ratio $\frac{[Ag^{\cdot}]_1}{[Ag^{\cdot}]_2}$ must be expressed in terms of $[NH_3]$. The latter concentration is found by first subtracting from the total NH_3 that part which is combined to form the simplest silver complex (combined $NH_3 = 2 \times [AgCl]$). The effective concentration $[NH_3]$ is now obtained by applying the empirical relation:

$$[NH_3] = C_{NH_3}(1 + 0{\cdot}08\, C_{NH_3}).$$

(2) In this case $[NH_3]$ is constant.

The concentrations of Ag^m, which are derived from the primary complex kations $[Ag_m(NH_3)_{m+1}]$, are obviously proportional to the concentrations of the latter by equation (3), Problem 90, p. 225.

Bodländer (*Zeitsch. physikal Chem.* (1902), 39, 598).

60. The dissociation pressure of Ag_2O is $5{\cdot}0 \times 10^{-4}$ atmospheres at 25°.

What is the E. M. F. of a cell :

$$\begin{array}{l|c|c} AgAg_2O & Ag_2O & O_2Pt \\ & \text{saturated solution} & \text{(1 atmosphere) ?} \end{array}$$

Answer **0·048** volt.

The reaction obviously involves the reduction of oxygen from atmospheric pressure to the dissociation pressure.

Lewis (*Zeitsch. physikal Chem.* (1906), 55, 465).

61. The affinity of the reaction :

$$H_2 + \tfrac{1}{2}\, O_2 \rightleftarrows H_2O$$

has been expressed by the equation :

$$A \text{ (cal.)} = 57{,}300 - 1{\cdot}75\, T \log T - 0{\cdot}0_33\, T^2 + 0{\cdot}457\, T$$
$$- 4{\cdot}56\, T \log \frac{p_{H_2O}}{p_{H_2} \times p_{O_2}^{\frac{1}{2}}}$$

Find the electromotive force of the cell which carries out this reaction at 25° and at 727° C.

Answer **1·178** and **0·981** volts.

Note $\dfrac{p_{H_2O}}{p_{H_2} \times p_{O_2}^{\frac{1}{2}}}$ is taken as 1

(See Gas Reactions.)

62. The electromotive force is required of an actual cell at 25°, in which

$$p_{H_2} = p_{O_2} = 0{\cdot}969 \text{ atmosphere} \qquad p_{H_2O} = 0{\cdot}031.$$

Answer $E = \mathbf{1{\cdot}222}$.

Haber ("Thermodynamics of Technical Gas Reactions," p. 326).

63. According to Nernst, the degree of dissociation of water-vapour at $t = 17°$ C. and $p = 1$ atmosphere is $0{\cdot}48 \times 10^{-25}$ per cent. (x). The pressure of saturated water-vapour at this temperature is 0·0191 atmosphere.

Find the electromotive force of the hydrogen oxygen cell, in which gaseous H_2 and O_2, each at atmospheric pressure, are combined to form saturated water-vapour, at 17°.

Answer $E = \mathbf{1{\cdot}25}$ volts.

(See Nernst ("Thermodynamics and Chemistry," pp. 113—117.)

$$A = 4\ EF = RT\Sigma n \log p \left(\frac{\text{reac.}}{\text{res.}}\right) - RT \log K_p \left(\frac{\text{reac.}}{\text{res.}}\right)$$

$$\log K_p = 3 \log x - \log 2.$$

64. The E. M. F. of a cell consisting of Pt/Br_2 ($p_{Br_2} = 1{\cdot}509$) and Pt/H_2 ($p_{H_2} = 753{\cdot}6$), electrodes in a solution of HBr, containing 0·925 gram of HBr in 1 c.c. ($p_{HBr} = 2{\cdot}25$), was found to be 0·625 volt, at 30° C.

Find the value of $K_p = \dfrac{p_{HBr}}{p_{H_2}^{\frac{1}{2}} \times p_{Br_2}^{\frac{1}{2}}}$

Answer $K_p = \mathbf{1{\cdot}95 \times 10^9}$.

65. What are the partial pressures of H_2 and Br_2 above acid of this concentration?

Answer $p_{H_2} = p_{Br_2} = \mathbf{1 \cdot 15 \times 10^{-9}}$.

Bodenstein and Geiger (*Zeitsch. physikal Chem.* (1904), 49, 70).

66. From the solubility product of $AgCl$ (Problem 44, p. 256) and the normal potentials Cl and Ag (Table, p. 237), find the electromotive force of the combination Cl_2 (atmospheric pressure) and 2 Ag, and the maximum work of their combination to $AgCl$, at 25°.

Answer $E = \mathbf{1 \cdot 135}$ volts

$A = \mathbf{52{,}360}$ calories.

For $$Ag,\ e = e_o + \frac{RT}{F} \log C_{Ag}.$$

The E. M. F. of the silver chlorine cell, at 20°, is found to be 1·13.

Katayama (*Zeitsch. physikal Chem.*, 61, 566).

The heat of formation of 2 mols. of $AgCl$ from Ag and Cl_2 is 58,760 calories (Thomsen).

67. The E. M. F. of the combination:

H_2Pt normal acid	normal salt	normal base H_2Pt
e.g. $N.\ HCl$	$N.\ NaCl$	$N.\ NaOH$

is 0·74 volt, at 18°.

The diffusion potentials are 0·0392 and 0·0262 volt opposed to the electrode potentials.

(See equation (3), p. 234.)

If the degree of dissociation of acid and base is 0·8, find the ionic product for water at 18°, and the hydrogen ion concentration in pure water.

Answer $\mathbf{1 \cdot 4 \times 10^{-14}}$ $\mathbf{1 \cdot 05 \times 10^{-7}}$.

The observed E. M. F. is due to the difference of [H·] in the two half cells. Since the [H·] in the acid half is known, that in the alkali half may be obtained from equation (2), p. 234.

68. A combination:

$$\begin{array}{c|c|c|c} Pt & FeCl_2 & N.\,KCl & HgClHg \\ & FeCl_3 & & \end{array}$$

has an electromotive force which is due to the affinity of the reaction:

$$Hg + Fe^{\cdot\cdot\cdot} + Cl' = Fe^{\cdot\cdot} + Hg^{\cdot} + Cl',$$

the mercury being oxidised by the ferric salt. The total difference of potential may be divided into the single potential of the calomel cell and the oxidation potential of the mixture of ferric and ferrous ions. The latter potential varies with the ratio of $[Fe^{\cdot\cdot\cdot}]$ to $[Fe^{\cdot\cdot}]$. At a certain value of this ratio the oxidation potential must be zero, and the total difference of potential therefore, 0·56 volt.

In the case investigated, solutions of $FeCl_3$ and $FeCl_2$, each 0·1 molar normal with respect to Fe were mixed in various proportions at 17°. It is assumed in the calculation that the ratio of $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$ is the same as the ratio of $FeCl_3$ to $FeCl_2$.

Per cent. total Fe present as $Fe^{\cdot\cdot\cdot}$	E
4	0·347
6	0·361
50	0·427

Find the equilibrium constant $\frac{Fe^{\cdot\cdot\cdot}}{Fe^{\cdot\cdot}}$ and the affinity of the oxidation when carried out by means of a solution normal with respect to both $Fe^{\cdot\cdot\cdot}$ and $Fe^{\cdot\cdot}$.

$$EF = \frac{RT}{n}\log K + \frac{RT}{n}\log\frac{[Fe^{\cdot\cdot\cdot}]}{[Fe^{\cdot\cdot}]}$$

(See equation (15), p. 237.)

Answer $\frac{Fe^{\cdot\cdot\cdot}}{Fe^{\cdot\cdot}} = \mathbf{2{\cdot}8 \times 10^{-7}}$.

$A = \mathbf{41{,}360}$ joules.

Peters (*Zeitsch. physikal Chem.* (1898), 26, 193).

See also Abegg and Maitland (*Zeitsch. Elektrochem.* (1906), 12, 263).

69. From the results of Problem 47, p. 41, find the electromotive force at 0° C. of the combination:

$$Hg\ HgCl \mid KCl \mid KOH \mid HgO\ Hg$$

which permits the reaction:

$$H_2 + HgO = H_2O + Hg$$

to proceed reversibly. See equation (7), p. 147.

The indeterminate constant ΣnC_i may be taken (1) as zero, (2) as — 1·5.

Answer $E = 0·92$ volt (1)
0·88 volt (2).

Nernst (*loc. cit.*, p. 41).

Brönsted (*Zeitsch. physikal Chem.* (1908), 65, 84).
Donnan and Allmand (*Journ. Chem. Soc.* (1911), 99 and 100, 855).

70. If it is assumed that $\frac{dA}{dt} = \frac{dU}{dt} = 0$ at the absolute zero of temperature, then it has been shown by Nernst ("Thermodynamics and Chemistry") that the free energy and total energy changes of a reaction between condensed phases may be represented by the equations:

$$q = q_o + b'T^2 + c'T^3$$
$$A = q_o - b'T^2 - c'T^3$$

(See Gas Reactions, Introduction, p. 147.)

The coefficients b' ($\Sigma nb'$) may be obtained as in Problem 47, p. 41.

The third and following terms of the power series may generally be omitted. (See Nernst. *loc. cit.*)

In cases where the coefficient b' is in itself small, the E. M. F. of the reaction may be calculated with considerable accuracy from the thermal data.

The heat of formation (1 mol.) of solid PbI_2 from the solid elements, is 39,800 calories. The specific heats at $T = 328$ are $Pb = 6·4$, $I = 6·86$ and $PbI_2 = 19·7$ per mol.

Find the numerical values of the above formulæ, A being expressed in volt-faradays for 1 equivalent.

Answer $q = 0{\cdot}863 + 0{\cdot}13 \times 10^{-7} T^2$

$$A = EF = E = 0{\cdot}863 - 0{\cdot}13 \times 10^{-7} T^2.$$

The coefficient b' found as in Problem 47, p. 41, for the gram molecule must be reduced to the corresponding value for the gram equivalent.

All quantities of energy must be divided by the appropriate factor.

$$2b'_S T = \Sigma n H_S \text{ (condensed reaction).}$$

71. Compare the E. M. F. of the Pb, I_2 element, at 290°, as deduced above, E_1 with the corresponding value E_2 obtained from the normal potentials of Pb and I, as in Problem 48, p. 257.

The solubility of PbI_2 is taken as 0·006 mol. per litre.

Answer $E_1 = 0{\cdot}863.$

$E_2 = 0{\cdot}86.$

The Lead Accumulator.

The electrical energy obtainable from a lead accumulator is, to a good approximation, equivalent to the work which would be obtained, if the concentrations and dilutions of the sulphuric acid observed during discharge were carried out reversibly by means of a piston mechanism.

The electromotive force of various combinations may therefore be calculated from the changes in the pressure of aqueous vapour over the dilute acids employed as electrolytes.

(See equation (4), p. 97.)

The following cases have been selected from the work of Dolezalek ("Lead Accumulator").

Let N be the number of molecules of H_2O to one of H_2SO_4, and p the saturation pressures of aqueous vapour.

Consider two complete accumulators containing acids of different concentration $C_1(N_1)$ and $C_2(N_2)$ working in opposition as in Problem 13, p. 242.

Then, if so much current is taken from the cell as corresponds to the transference of 1 mol. of water, the maximum work associated with this and the necessary reversed transference of H_2SO_4 can be shown to be:

$$\frac{RT}{F}\left(N_2 \log p_2 - N_1 \log p_1 - \int_{N_1}^{N_2} \log p dN + \log \frac{p_2}{p_1}\right)$$

The difference between the E. M. F.'s at 0° C. of two accumulators, containing respectively 3 and 10 mols. of H_2O to 1 of H_2SO_4, and having aqueous vapour pressures of 0·431 and 2·975 mm. of mercury, has been calculated by Dolezalek. The value obtained, 0·28 volt, agrees well with the experimental value, and with that obtained from the reaction heats.

(See Problem 14, p. 243.)

72. The electromotive force may also be calculated indirectly in many ways of which the following is a specimen.

The total work furnished by a pair of accumulators, as above, may be divided into two parts, the first due to the transference of H_2O,

$$\frac{RT}{nF} \log \frac{p_2}{p_1};$$

the second due to the transference of H_2SO_4.

$$\frac{RT}{nF}\left(N_2 \log p - N_1 \log p - \int_{N_1}^{N_2} \log p dN\right).$$

Let the expression in brackets be abbreviated to $f(p)$.

The electromotive force of a Pb concentration cell with migration similar to that described in Problem 17, p. 243, is:

$$E' = 0{\cdot}99 \times 10^{-4} T v_K f(p);$$

while that of the PbO_2 cell with migration (Problem 19, p. 244) is:

$$E'' = 0{\cdot}99 \times 10^{-4}\, T\left[(2 - \nu_K)\ f(p) + \log\frac{p_2}{p_1}\right]$$

ν_K being the migration number of $H^{\cdot}$ as stated in the problem referred to.

The E. M. F. of the Pb, $PbSO_4$ combination containing acids of $C_1 = 0{\cdot}2$ per cent. H_2SO_4 ($p = 15{\cdot}3$ mm.) and $C_2 = 36{\cdot}5$ per cent. H_2SO_4 ($p = 10{\cdot}0$ mm.) is 0·14 volt.

What is the difference in electromotive force between two complete accumulators, the one containing C_1, the other C_2, per cent. H_2SO_4?

Answer $E =$ **0·348** volt.

73. If the accumulator acid is dilute, the degree of dissociation and the relation between the osmotic pressure and the acid concentration remains fairly constant, at different concentrations. In this case, the osmotic work, when current flows, may be calculated from the transport numbers and the numbers of ions migrating from regions of higher (C_2) to lower (C_1) concentrations.

Thus, from the results of the preceding problems, p. 271, find an expression for the E. M. F. of the Pb and PbO_2 concentration chains containing acids of concentrations C_2 and C_1.

(See Problems 17 to 19, pp. 243, 244.)

Answer (Pb chain) $E_1 = i\,\frac{RT}{2F}\,\nu_K \log\frac{C_2}{C_1}$ . . (1)

(PbO_2 chain) $E_2 = i\,\frac{RT}{2\,F}\left[(2 - \nu_K)\log\frac{C_2}{C_1} + \frac{i(C_2 - C_1)}{2{\cdot}3\,N}\right]$ (2)

The last term in brackets in equation (2) is derived from the transport of 2 mols. of H_2O for 2 F. $2\,EF = RT \log \frac{p_2}{p_1}$, and $\log\frac{p_2}{p_1} = \frac{i(C_2 - C_1)}{N}$. $N =$ mols. of H_2O to 1 of H_2SO_4.

(See Problem 24, p. 106.)

Hence, show that, at 17°, at which temperature $i = 2{\cdot}22$, $\nu_K = 0{\cdot}85$.

$$E_1 = 2{\cdot}22 \times 0{\cdot}99 \times 10^{-4} \times 290 \times 0{\cdot}85 \log \frac{C_2}{C_1}.$$

$$E_2 = 2{\cdot}22 \times 0{\cdot}99 \times 10^{-4} \times 290 \left[1{\cdot}15 \log \frac{C_1}{C_2} + 0{\cdot}017\,(C_2 - C_1)\right].$$

74. If $C_2 = \frac{3}{8}$, and $C_1 = \frac{3}{32}$ mols. per litre, find the E. M. F. (positive potential of the electrode in C_2 — that in C_1) in the case of the Pb and PbO_2 electrodes.

Answer — **0·0329** volt.
+ **0·0446** „

75. By how much does the electromotive force of a Pb concentration chain differ from that of a PbO_2 concentration chain, when the concentrations of acid in the two halves of each are $\frac{3}{16}$ and $\frac{3}{32}$ mol. per litre?

Answer The PbO_2 cell has an E. M. F. higher by **0·0059** volt.

76. What will be the joint E. M. F. of the combination of Pb and PbO_2 cells, if the dilute acid PbO_2 is connected to the dilute acid Pb electrode?

$$PbO_2(C_2)\ PbO_2(C_1)\ Pb(C_1)\ Pb(C_2).$$

Draw a diagram as on p. 247 to illustrate the steps of potential.

Answer **0·0389** volt.

77. From these equations, a formula may be deduced which gives the alteration of electromotive force of a whole accumulator with concentration (gram molecules per litre).

$$E = \frac{iRT \times 2{\cdot}3}{2F}\left[2 \log \frac{C_2}{C_1} + 0{\cdot}016\,(C_2 - C_1)\right].$$

If $E = 1{\cdot}92$ volts for an accumulator containing 1 N. acid, find E for an accumulator containing 0·111 N. acid.

Answer $E =$ **1·80** volts.

If the Pb and PbO_2 equations are added, and the numerical values introduced ($T = 290°$) an equation may be obtained of the form:

$$E_c = 1·92 + a \log C + bC.$$

It has been evident from the preceding problems that the energy changes associated with the charge and discharge of a lead accumulator can be regarded as reversible. The condition of reversibility is that all reactions are carried out very slowly. The rapid charging and discharging, however, which are necessary in practice are associated with considerable irreversible effects which have to be introduced into the energy equations in some such way as that outlined below. (See Dolezalek, *loc. cit.* p. 244.)

78. Let E_d, I_d; E_c, I_c be the discharging and charging E. M. F. and current of a given battery, t, the times, and Q the extra energy spent in charging beyond that obtained in discharging. This loss of energy, mainly due to an increased voltage depending on the changes in acid concentration at the poles, appears as heat evolved on irreversible mixing of the concentration layers (chiefly in the pores of the active mass).

$$\text{The efficiency } (\epsilon) = \frac{\int_{t_o}^{t_1} E_d I_d d_t}{\int_{t_o}^{t_1} E_c I_c d_t},$$

And $Q = KI^2t$, since the loss of energy behaves as if due to high resistance and appears as heat.

K is a constant for a definite quantity of active material.

The mean electromotive force of some accumulators during discharge was 1·925 volts, and the current was 152·7 amperes for 4·5 hours. In order to charge again, the following quantities were required:—(1) 134·3 amperes at 2·30 volts for 5·4 hours; (2) 139·6 amperes at 2·35 volts for 5·5 hours.

Find the efficiency, the loss of energy and the mean value of the constant K.

Answer $\epsilon = \mathbf{0{\cdot}79}$.

$Q = \mathbf{350}$ and $\mathbf{480}$.

$K = \mathbf{0{\cdot}00405}$.

$$2{\cdot}30 \times 5{\cdot}4 \times 134{\cdot}3 = 1{,}670.$$

$$\frac{1{,}320}{1{,}670} = 0{\cdot}79.$$

$$1{,}670 - 1{,}320 = Q = 350.$$

$$K = \frac{Q}{I^2t} = 0{\cdot}0036, \text{ etc.}$$

79. What is the efficiency of the whole process, if the cell is discharged as in the first case considered above, but charged at 145 amperes, in 5 hours?

Find the E. M. F. required for charging.

Answer $\epsilon = \mathbf{0{\cdot}76}$

$E = \mathbf{2{\cdot}408}$ volts.

KINETICS OF MOLECULAR AND RADIOACTIVE CHANGES.

Symbols and Definitions.

The following symbols have been used:

C_1, C_2, etc., for concentrations of reacting molecules.

C'_1, C'_2, etc., for concentrations of resulting molecules.

C_o for the concentration at the beginning of a reaction.

The differential $-\dfrac{dc}{dt}$ expresses the rate of decrease of concentration of the reacting molecules present at any moment.

The rate of decrease of each molecular species is proportional to the concentrations of the reacting molecules, each raised to a power equal to its numerical coefficient in the stoichiometrical equation.

Thus, if :

$$n_1A_1 + n_2A_2 + n_3A_3 \rightleftarrows n'_1A'_1 + n'_2A'_2 + n'_3A'_3$$

$$-\frac{dC}{dt} = k_1(C_1{}^{n_1} \times C_2{}^{n_2} \times C_3{}^{n_3}).$$

And for the reverse reaction

$$-\frac{dC}{dt} = k_2C'_1{}^{n'_1} \times C'_1{}^{n'_2} \times C'_3{}^{n'_3}.$$

The constants k_1 and k_2 are called the velocity constants for the direct and reverse reactions.

Or, if x is the amount of each molecular species changed at the end of the time t, and the molecules are present initially at concentrations a and b :

$$\frac{dx}{dt} = k_1\,(a - x)\,(b - x).$$

Complete or Irreversible Reactions.

Unimolecular. $A \longrightarrow A'$

$$-\frac{dC}{dt} = kC \quad . \quad . \quad . \quad (1)$$

$$\begin{aligned} {}^*-\log C &= kt + C_i \\ \underline{-\log C_o} &\underline{= \qquad C_i\,(t = 0)} \end{aligned}$$

$$\text{subtracting, } \log\frac{C_o}{C} = kt \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\log\frac{C_1}{C_2} = k(t_2 - t_1) \; . \quad . \quad . \quad . \quad (3)$$

Bimolecular. $A_1 + A_2 \longrightarrow A'_1 + A'_2$.

Let the reacting substances be present in the same initial concentrations

$$-\frac{dC}{dt} = kC^2 \quad . \quad . \quad . \quad (4)$$

---

* The true velocity constant of the differential equation is of course obtained by multiplying the ordinary logarithms in equation (2) by 2·303. The use of a constant $k' = \frac{k}{2{\cdot}303}$ obviously reduces the amount of computation required, and is permissible in most cases.

$$\int -\frac{dC}{C^n} = \frac{C^{-n+1}}{-n+1}. \quad \text{(See p. 5.)}$$

$$\frac{1}{C} - \frac{1}{C_o} = kt \quad . \quad . \quad . \quad (5)$$

$$\frac{1}{C_2} - \frac{1}{C_1} = k(t_2 - t_1) \quad . \quad . \quad . \quad (6)$$

Polymolecular $A_1 + A_2 + A_3 \longrightarrow A'_1 + A'_2 + A'_3$

$$-\frac{dC}{dt} = kC^n \quad . \quad . \quad . \quad (7)$$

$$\frac{1}{n-1}\left(\frac{1}{C^{n-1}} - \frac{1}{C_o^{\,n-1}}\right) = kt \quad . \quad . \quad (8)$$

$$\frac{1}{n-1}\left(\frac{1}{C_2^{\,n-1}} - \frac{1}{C_1^{\,n-1}}\right) = k(t_2 - t_1) \quad . \quad (9)$$

Bimolecular. The reacting substances are present in different initial concentrations

$$-\frac{dC}{dt} = kC_1 \cdot C_2 \quad . \quad . \quad . \quad (10)$$

Let ${}_oC_1$ and ${}_oC_2$ be the initial concentrations of the two kinds of molecules, and let C_1 and C_2 be the concentrations after the lapse of time t.

Then $$k = \frac{1}{({}_oC_1 - {}_oC_2)t} \log \frac{C_{1\,o}C_2}{C_{2\,o}C_1} \quad . \quad . \quad (11)$$

or calling the constant difference between ${}_0C_1$ and ${}_0C_2$ "a":

$$k = \frac{1}{at} \log \frac{C_1({}_oC_1 - a)}{{}_oC_1(C_1 - a)} \quad . \quad . \quad (12)$$

Or, if a and b are the concentrations present at the beginning and x is transformed at the end of time t:

$$k = \frac{1}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \quad . \quad . \quad (13)$$

Radioactivity.

The activity of a radioactive substance is proportional to the rate of change of the molecules which give rise to the measured radiation. A definite fraction of the total number (N) of molecules is ready to change at any given time:

$$-\frac{dn}{dt} = kN \quad . \quad . \quad . \quad (1)$$

Rate of Decay.

An active substance B in changing into the next disintegration product C gives off a radiation of intensity I at the beginning, and a radiation of intensity I_t at the end of a period of time t, during which B is isolated from the parent substance A.

$$\text{Then } \log\frac{I_t}{I} = -kt \qquad \frac{I_t}{I} = e^{-Kt}. \quad . \quad . \quad (2)$$

Rate of Recovery.

Let the active product B give a radiation of intensity I when it is present in equilibrium quantity, *i.e.*, when it is being produced from A at the same rate at which it is being converted into C. If A is completely deprived of C, the activity will be zero. The recovery of activity due to the formation of new B is given by the equation:

$$\frac{I_t}{I} = 1 - e^{-kt} \quad . \quad . \quad . \quad (3)$$

or if kt is small:

$$\frac{I_t}{I} = kt \quad . \quad . \quad . \quad . \quad (4)$$

k has the same numerical value as in equation (2).

Rutherford ("Radioactivity," pp. 224, 225).

Number of Molecules and "Life" of a Radioactive Substance.

If n_o are the number of molecules charging in unit time, and N_o the number of molecules present at any time, then for a relatively slow change:

$$-\frac{dn}{dt} = -\frac{\Delta n}{\Delta t} = n_o = kN_o.$$

The constant k is the same as that obtained from equations (2) and (3),

$$k = \frac{n_o}{N_o} \quad . \quad . \quad . \quad . \quad (5)$$

This is the physical meaning of the radioactive constant K. It expresses the ratio between the number of molecules changing per unit of time and the total number present.

If n_o and N_o refer to the state of radioactive equilibrium, then by the preceding n_o is also equal to the number of molecules of B produced per unit of time.

The "life" a radioactive product may be defined as the time required for the activity to fall from its initial to one half its initial value.

The initial activity is that which the product has when present in the greatest possible quantity, *i.e.*, when it is in equilibrium with its parent substance.

The numerical value of the "life" is evidently given by the equation:

$$\log 2 = kt_{\frac{1}{2}} \quad . \quad . \quad . \quad (7)$$

k having been obtained from equation (2) (decimal logarithms).

Note.—Some of the original results have been modified by further investigations. The method of treatment, however, as illustrated by the examples chosen, remains unaltered in its essentials.

Incomplete Reactions.

Unimolecular $A \rightleftarrows A'$.

Suppose at the end of time t, x of A has been transformed into A':

$$\frac{dx}{dt} = k_1 (a - x) - k_2 x, \quad . \quad . \quad (1)$$

where $\frac{dx}{dt}$ is the net velocity, or actual velocity observed at time t.

At equilibrium $$\frac{dx}{dt} = 0.$$

Let the amount of A transformed at this point be ξ.

Then $$k_1(a - \xi) = k_2\xi,\ k_2 = k_1\frac{a-\xi}{\xi} \quad . \qquad (2)$$

Substituting (2) in (1):

$$\frac{dx}{dt} = \frac{k_1a(\xi - x)}{\xi} \quad . \quad . \qquad (3)$$

$$\int\frac{dx}{\xi - x} = \log\frac{\xi}{\xi - x} = \frac{a}{\xi}k_1t = k't; \quad . \qquad (4)$$

in which k' is a constant for any particular original mixture.

Or, substituting for k_1 in (4) its value from (2):

$$\log\frac{\xi}{\xi - x} = \frac{a}{a - \xi}k_2t. \quad . \quad . \qquad (5)$$

From (4) and (5):

$$\frac{1}{t}\log\frac{\xi}{\xi - x} = k_1 + k_2. \quad . \quad . \qquad (6)$$

Similarly for the reverse reaction $A' \longrightarrow A$

$$\frac{dx}{dt} = k_2(a - x) - k_1x \quad . \quad . \qquad (1\text{A})$$

$$\frac{dx}{dt} = \frac{k_1a(a - \xi - x)}{\xi}$$

$$\int\frac{dx}{a - \xi - x} = \log\frac{a - \xi}{a - \xi - x} = \frac{a}{\xi}k_1t \quad . \qquad (5\text{A})$$

From (2) $$\frac{a}{\xi} = \frac{k_1 + k_2}{k_1}$$

$$\therefore\ \log\frac{a - \xi}{a - \xi - x} = (k_1 + k_2)t. \quad . \qquad (6\text{A})$$

If K is the equilibrium constant $= \dfrac{k_1}{k_2}$,

$$K = \frac{\xi}{a - \xi} \qquad \therefore\ \xi = \frac{a - K}{1 + K} \quad . \qquad (7)$$

Substitute (7) in (6)

$$\log\frac{aK}{aK - (1 + K)x} = (k_1 + k_2)t. \quad . \qquad (8)$$

Bimolecular $A_1 + A_2 \rightleftarrows A'_1 + A'_2$.

If C_1, C_2, and C'_1, C'_2 are the concentrations at any time, then the net velocity $\frac{dx}{dt}$ at this time may be found from the velocity constants k_1 and k_2 of the direct and the reversed reactions.

$$-\frac{dC}{dt} = k_1C_1C_2 - k_2C'_1C'_2 \quad . \quad . \qquad (9)$$

Or, if a and b are the amounts of the reactants at the beginning, and x is changed after time t:

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2x^2 \quad . \qquad (10)$$

If ξ is the value of x at equilibrium:

$$\frac{k_1}{k_2} = K = \frac{\xi^2}{(a - \xi)(b - \xi)} \quad . \qquad (11)$$

For a fuller treatment of this and other cases see Mellor ("Chemical Statistics and Dynamics," p. 88).

Order of a Reaction.

The best evidence that a reaction is uni-, bi-, or polymolecular (of the 1st, 2nd, or nth order) is derived from the velocity results themselves.

A most obvious and useful way of determining the order is to calculate the velocity on each of the foregoing assumptions. Of the k values so obtained, one series will usually be more constant than the rest.

Among other methods of finding the order of a reaction are the following:

(1) The differential method (Van't Hoff).

If the differential $-\frac{dC}{dt}$ can be determined with different initial concentrations, C_1 and C_2; then:

$$-\frac{dC_1}{dt} = kC_1^n$$

$$-\frac{dC_2}{dt} = kC_2^n.$$

Taking logarithms, and subtracting (2) from (1):

$$n = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2} \quad . \quad . \qquad (1)$$

The differential $\frac{dC}{dt}$ may sometimes be obtained with sufficient accuracy from the small finite differences in time and concentration:

$$\frac{\Delta C}{\Delta t}.$$

(2) The method of finding the times required for equal fractional decreases of concentration (Ostwald, Noyes).

Let two experiments be made with different initial concentrations, C_1 and C_2 of the reacting substance:

C_1 decreases to C'_1 in time t_1
C_2 ,, ,, C'_2 ,, ,, t_2.

C_1 and C_2 are so chosen that:

$$\frac{C'_1 - C_1}{C_1} = \frac{C'_2 - C_2}{C_2}.$$

Let k_1 and k_2 be the velocity constants of the reaction as measured from C_1 and C_2; then by means of equation (9), p. 277, and algebraical transformations, it can be shown that:

$$\left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C'_2}{C'_1}\right)^{n-1} = \frac{k_1 t_1}{k_2 t_2} \text{ (Ostwald).}$$

(See Mellor, "Chemical Statistics and Dynamics," p. 62.)

If the reaction follows the same course throughout, then:

$$k_1 = k_2,$$

$$\therefore \quad n = 1 + \frac{\log t_1 - \log t_2}{\log C_2 - \log C_1} \text{ (Noyes).}$$

(3) Method of isolation (Ostwald).

From the equation:

$$-\frac{dC}{dt} = k(C_1^{n_1} \times C_2^{n_2} \times C_3^{n_3}),$$

it is evident that if the concentrations C_2 and C_3 are very large compared to C_1, the whole reaction will appear to be of the nth order:

$$-\frac{dC}{dt} = kC_1^{n_1}.$$

The exponents n_2 and n_3 are similarly determined.

Velocity of Diffusion.

The observed velocity of a reaction in a heterogeneous system is often dependent upon the velocity of diffusion of one of the reacting molecular species across the surface separating the phase of constant composition (pure solid) from the phase of variable composition (solution).

Examples of such reactions are: the diffusion of a salt down a concentration gradient, followed by hydration and ionisation, and the diffusion of hydrogen or metal ions to a metallic surface, followed by an interchange of ionic charges.

The amount of a substance Δx transformed in each interval of time Δt is proportional to:

(1) The surface of separation S of the phases. (2) The rate of diffusion of active material, to or from each unit of area of the surface. The rate of diffusion $\frac{\Delta x}{\Delta t}$, from a constant surface is proportional to the concentration gradient $\frac{dc}{dl}$ (rate of decrease of concentration across the surface of separation), and to the specific diffusion coefficient k_D.

Thus
$$\frac{\Delta x}{\Delta t} = k_D S \frac{dc}{dl} \quad . \quad . \quad . \quad (1)$$

k_D is defined as the amount of substance Δx diffusing in each unit of time, when S and $\frac{dc}{dl}$ are each equal to unity.

If $\frac{dc}{dl}$ is constant during the time of experiment:

$$\frac{\Delta x}{\Delta t} = k \quad . \quad . \quad . \quad . \quad (2)$$

Consider the case of the solution of a salt in water. The concentration of the salt is C in the solution; C_S (saturated) in contact with the solid phase, and the concentration gradient is therefore $\frac{C_S - C}{l}$, if l is the thickness of the diffusing layer which surrounds the salt.

$$\frac{\Delta x}{\Delta t} = k_D S \frac{C_S - C}{l} \quad . \quad . \quad . \quad (3)$$

If the volume of the solution V is large, $C_S - C$ remains practically constant with a constant rate of stirring.

$$\frac{\Delta x}{\Delta t} = kS \quad . \quad . \quad . \quad . \quad (4)$$

If the volume of the solution V varies, *e.g.*, on the removal of test-samples, and the change measured by the titration of these is the change in concentration ΔC, it is evident that:

$$\frac{\Delta C}{\Delta t} = \frac{\Delta x}{\Delta t} \cdot \frac{1}{V} \qquad V \cdot \frac{dC}{dt} = \frac{dx}{dt}$$

Substituting in equation (3)

$$\frac{\Delta C}{\Delta t} = \frac{k_D S}{V} \cdot \frac{C_S - C}{l} \quad . \quad . \quad . \quad (5)$$

The constant for any particular case follows from the integrated form:

$$\left.\begin{aligned} \frac{k_D S}{Vl} &= \frac{1}{t} \log \frac{C_S}{C_S - C} \times 2{\cdot}303 \\ \text{or} \qquad & \frac{1}{t_2 - t_1} \log \frac{C_S - C_1}{C_S - C_2} \times 2{\cdot}303 \end{aligned}\right\} \quad . \quad (6)$$

The terms accessible to measurement on the left-hand side are obviously the volume of the solution and the surface of the diffusing layer.

The velocity of solution is found to vary with the rate of stirring, because this will in all probability affect the thickness l of the diffusing layer.

In what follows, the remaining constant k is assumed to be identical with the diffusion constant as defined in equation (1).

PROBLEMS.

Complete Reactions.

1. If x of a substance originally present at concentration "a" is transformed at the end of time t, show by integration (equation (2), p. 276), that:

$$\log \frac{a}{a-x} = kt$$

$$\text{and } \log \frac{a-x_1}{a-x_2} = k(t_2 - t_1).$$

The concentration of the reacting molecules of a given system was 10 at the commencement; after a certain time, 2·818, and after a further 1 hour and 40 minutes, 1·778.

Find the reaction constant k of the differential equation (t in minutes); the time elapsing from the commencement until the concentration is 2·818, and the fraction of the original amount which remains unchanged at $t = \frac{1}{k}$.

$$\text{Answer} \quad k = \frac{2{\cdot}303}{t_2 - t_1} \log \frac{C_1}{C_2} = 0{\cdot}004606$$

$$0{\cdot}002 = \frac{1{\cdot}0 - 0{\cdot}45}{t_1 - 0}$$

$$t_1 = 275 \text{ minutes.}$$

$$Kt = 1 = 2{\cdot}303 \log \frac{1}{1-x} \qquad 1 - x = \text{unchanged fraction.}$$

$$2{\cdot}303 \log (1-x) = -1.$$

$$1 - x = \frac{1}{e}.$$

2. A 20 per cent. solution of cane sugar having a dextrorotation of 34°·50 is inverted by 0·5 normal lactic acid, at 25°. The rotation at the end of 1,435 minutes is + 31°·10; at the end of 11,360 minutes, + 13°·98, and after complete inversion, − 10°·77.

Show that the reaction follows the unimolecular law, and calculate the constant of the differential equation from the two measurements.

Answer $K = 0\cdot544 \times 10^{-4}$ and $0\cdot532 \times 10^{-4}$.
(natural logarithms).

The fraction inverted at any time may be calculated by proportional parts as in Problem 3, p. 99.

Thus, if ϕ_r and ϕl are the rotations of the inverted and uninverted sugar, ϕ_x the rotation at any time t, and x the concentration of inverted sugar at this time:

$$\frac{Co}{Co - x} = \frac{\phi_r + \phi_l}{\phi_x + \phi_l}$$

ϕ_r and ϕ_l are merely the numerical values, but ϕ_x is given its proper sign.

3. Assuming that the velocity constant has the same value in a more dilute sugar solution of the same acid concentration, calculate how much will be inverted in 50 hours, and how much left unchanged after 500 hours in 1 litre of a 15 per cent. solution of cane sugar, at 25°.

$$\log \frac{C_o}{C_o - x} = \frac{k \times t\,(\text{min.}),}{2\cdot303}$$

k having the value found in the last problem.

Answer 22·30 grams inverted in 50 hours.
29·80 grams left after 500 hours.

4. AsH_3 (gas) $= As$ (solid) $+ 3\,H$.

This is one of the few gas reactions, the velocity of which has been successfully studied. The amount of decomposition may be deduced from the change of pressure at constant volume.

Let P_o and P be the total pressures at $t = 0$ and $t = t$, C_o and C, the corresponding concentrations of AsH_3, and x the fraction of the original gas decomposed at t.

Show that $\frac{P}{P_o} = 1 + \frac{x}{2} \qquad x = \frac{2\,P}{P_o} - 2,$

and hence $\frac{C}{C_o} = 3 - \frac{2\,P}{P_o}.$

The initial pressure being 784·84 millimetres, which rose to 878·50 mm. in 3 hours, find x and k (t in hours.)

Answer $x = \mathbf{0{\cdot}466}$.

$$k = \frac{1}{t} \log \frac{C_o}{C} = \frac{1}{t} \log \frac{P_o}{3\,P_o - 2\,P} = \mathbf{0{\cdot}0908}.$$

5. The mean velocity constant of the above reaction was found to be 0·0906. Find the time at which AsH_3 (originally under a pressure of 2 atmospheres) will be half decomposed, and the pressure then prevailing.

$$\frac{P}{P_o} = \frac{N}{N_o}$$

Answer $P = \mathbf{2\tfrac{1}{2}}$ atmospheres.

$$t_{\frac{1}{2}} = \frac{0{\cdot}3010}{k} = \mathbf{3{\cdot}3} \text{ hours.}$$

6. At a temperature of 367° C. k for the decomposition of $AsH_3 = 0{\cdot}202$ (decimal logarithms, and time in hours). How many molecules per cent. will be decomposed, when the velocity has fallen to one half its original value, and during the fifth half hour?

The original concentration is 1

$$-\frac{dC}{dt} = kC = 0{\cdot}202 \qquad 0{\cdot}101 = 0{\cdot}202 \times C.$$

Answer (1) **50** per cent.
(2) **6·48** per cent.

$$2{\cdot}303 \log \frac{1 - x_1}{1 - x_2} = k\,(t_2 - t_1).$$

$$2{\cdot}303 \log \frac{1}{1 - x_1} = k\,(t_1 - 0).$$

From these equations the values of log $(1 - x)$, and $-$ log $(1 - x_2)$ may be obtained.

7. It was found by Wilhelmy that out of 10·023 grams of cane sugar dissolved in 89·977 grams of water, 3·726 grams were inverted in 130 hours. Find the constant for the reaction considered as unimolecular, and as bimolecular.

Also, apply the unimolecular and bimolecular equation to find the percentage of the original amount of sugar inverted in two hours, in the case of a solution containing 1 gram of sugar in 100 grams of water.

Answer $k = 0{\cdot}001552$ unimolecular.
$(a - b)\,k = 0{\cdot}001548$ bimolecular.
0·72 per cent. unimolecular.
0·87 per cent. bimolecular.

Using the unimolecular equation :

$$0{\cdot}00155 = \tfrac{1}{2} \log \frac{1}{1 - x}.$$

Hence $1 - x$ and $100\,x$.

Using the bimolecular equation :

$$k = \frac{1}{(a - b)t} \log \frac{b\,(a - x)}{a\,(b - x)}$$
$$= \frac{1}{(b - a)t} \log \frac{a\,(b - x)}{b\,(a - x)}$$

Note the number of grams of water disappearing for every gram of cane sugar inverted.

$$(b - a)\,k = \frac{(b - a)\,k}{79{\cdot}954} = \frac{1}{t} \log \frac{1 \times (100 - x)}{(1 - x)\,100}$$

8. What times will be required to invert 25 per cent. of the sugar in a solution containing 10 grams of sugar and 100 grams of water, according as the reaction proceeds in a unimolecular or bimolecular manner?

Answer 80·58 hours.
71·22 hours.

9. Suppose that the two reacting kinds of molecules in a bimolecular reaction are not present in equivalent quantities at the beginning of the reaction. The velocity constant and time are then given by equations (11), (12), and (13), p. 277.

The saponification of ethyl acetate by means of $NaOH$ was investigated by Reicher.

$$NaOH + CH_3COO_2H_5 = CH_3{\cdot}COONa + C_2H_5OH.$$

See Van't Hoff ("Chemical Dynamics")

One hundred cubic centimetres of the reacting mixture were run at known intervals of time into a known excess of standard H_2SO_4, and titrated back with standard $Ba(OH)_2$.

The above equation can easily be adapted to the cases in which the alkali or the ester are in excess. It is, of course, the concentration of the former which is actually measured.

Let C_o C_t and C_f represent the concentrations of that reactant which is in excess, at the beginning, after time t, and at the end of the reaction, respectively.

Let C'_o and C'_t represent the concentrations of the reactant which is not in excess.

Then $$C_f = C'_o - C_o$$

and $$kt = \frac{1}{C_f} \log \frac{C_t \cdot C'_o}{C_o \cdot C'_t}$$

(1) Let the reactant, of which the concentration is actually measured, be in excess.

$$kt = \frac{1}{C_f} \log \frac{C_t(C_o - C_f)}{C_o(C_t - C_f}$$

$$k\,(t_2 - t_1) = \frac{1}{C_f} \log \frac{C_{f_2}(C_{t_1} - C_f)}{C_{t_1}(C_{t_2} - C_f)}$$

(2) Let the ester be in excess.

C_f of the ester is now left at the end of the reaction.

$$kt = \frac{1}{C_f} \log \frac{(C'_t + C_f)\,C'_o}{(C'_o + C_f)\,C'_t}$$

The experimental results were as follows :

The first column contains the times (in minutes) which have elapsed since the beginning of the reaction.

The second column contains the number of cubic centimetres of baryta (of the stated strength) equivalent to the alkali in 100 c.c. of the reacting mixture.

The unit of concentration used in calculating the constant is 1 gram equivalent in the litre, or 1 c.c. of normal baryta to 1 c.c. of the reacting mixture.

t	C.c. $Ba(OH)_2$
0	61·95
4·89	50·59
11·36	42·40
29·18	29·35
∞	14·92

Litre of $Ba(OH)_2$ $= \frac{1}{22{\cdot}797}$ normal.

If C is the concentration, N the normality of the baryta, and V the number of cubic centimetres used,

$$C = 0{\cdot}01\ N.$$

Find the constant of this reaction.

Answer $k = \mathbf{2{\cdot}31}$.
$k = \mathbf{2{\cdot}28}$.
$k = \mathbf{2{\cdot}28}$.

10. In two other experiments there was (1) excess of alkali; (2) excess of ester.

(1)

t	c.c. $Ba(OH)_2$
0	62·09
3·74	54·33
∞	33·06

Standard of baryta $= \frac{N}{24{\cdot}07}$

(2)

t	c.c. $Ba(OH)_2$
0	38·94
2·52	31·32
∞	23·65

Standard of baryta $= \frac{N}{24{\cdot}07}$

Find the reaction constant in each case, and compare the times required to saponify half a gram equivalent of the ester.

Answer $k = \mathbf{3{\cdot}47}$.
Time = **6·72** minutes (1).
4·47 minutes (2).

11. If the velocity constant of the above reaction, expressed in the same units, but at another temperature is 4·0, compare the times required to transform 50 per cent. of the ester in two solutions: (1) originally $\frac{1}{100}$ normal; (2) originally $\frac{1}{25}$ normal, with respect to ester and alkali.

What would be the error in minutes, if the time required for the second transformation were calculated from the time required for the first, on the assumption that velocities are simply proportional to concentrations?

Answer **250** minutes.
62·5 minutes.
The difference so calculated would be **187·5** minutes, instead of **243·75** minutes.

12. In the case of the $\frac{1}{25}$ normal mixture, how much ester in the litre is saponified during the fifth, and during the tenth minute, from the commencement?

(See equation (5), p. 277.)

Answer **0·00217** equivalents during the fifth minute.
0·00101 equivalents during the tenth minute.

13. In the last problem, show that, if the initial concentration were 1·0, the time required for the transformation of one half is $\frac{1}{k} = \mathbf{15}$ seconds.

14. From the data of Problem 35, p. 304, find the velocity constant of the oxidation of $FeCl_2$ by $KClO_3$ and HCl.

Taking results (2) and (3), and (5) and (6),

$$k = 1·06$$
$$= 0·92.$$

Answer $k =$ **1·0** approximately.

Radio-active Changes.

15. The activity of thorium X (active product of thorium disintegration) when isolated from the parent thorium falls to one half its value in four days.

What is the radioactive constant (t in hours), and how much time will elapse before the activity decreases to one-sixth of its maximum value? (See equation (2), p. 276.)

Answer $k = \mathbf{0{\cdot}0072}$

$t = \mathbf{10}$ days.

$$2{\cdot}303 \log 2 = kt = k \times 96$$

$$2{\cdot}303 \log 6 = kt \qquad t = 249 \text{ hours.}$$

16. The radioactive constant for the change: radium emanation ⟶ next product being $\frac{1}{463000}$ (t in seconds), find the time required for the activity of a sample of the emanation to fall from 100 to 20.

Curie (Compt. rend. (1902), 135, 857); Rutherford and Soddy (*Phil. Mag.*, April, 1903).

Answer **207** hours.

$$2{\cdot}303 \log 5 = \frac{1}{463{,}000} \times 3{,}600\ t.$$

17. The active thorium (thorium X) may be separated from the parent thorium by precipitation with ammonia, the active part remaining in the filtrate.

The inactive thorium is allowed to stand for a definite time; the thorium X formed in this time is again separated by precipitation, and the radioactivity measured. It is given by equations (3) and (4), p. 278, I being the total activity of thorium X when there is radioactive equilibrium.

The value of k has been already deduced from the decay of the activity (Problem 15).

Find the time required to produce one-sixth of the full activity I from a sample of thorium which has been deprived of thorium X.

What fraction of the maximum activity I will be recovered in 1 hour, and in 5 days?

Answer **21·5** hours.

$\frac{\mathbf{1}}{\mathbf{140}}$ of I.

0·5 of I.

For the short periods of time, 1 hour and 1 day, the approximate method of calculation, equation (4) may be used; for the longer period, however, the more exact equation (3) is preferable.

Plot the curves of decay and recovery of activity, using the constant found above, activities (ordinates) being given as percentages of I (100) and the times (abscissæ) being in days.

Rutherford and Soddy (*Phil. Mag.*, September, 1902).

Note.—On account of the formation of emanation, and for other reasons, there are considerable irregularities in the initial periods of decay and recovery, and the recovery appears to commence from a minimum and not from zero activity.

Rutherford ("Radioactivity").

18. The activity of some thorium emanation fell to one-half its initial value in 60 seconds. What is the radioactive constant and the ratio between the total number of emanation atoms and those changing in each unit of time, when the emanation and its parent thorium X are in radioactive equilibrium?

Answer $k = \mathbf{0{\cdot}0116} \qquad n_0 = \mathbf{0{\cdot}0166}\ N_0$

$$\frac{N_o}{n_o} = 87$$

$$k = 2{\cdot}3 \times \frac{0{\cdot}3010}{60}$$

19. Some $RaCl_2$ (0·03 gram) of activity, one thousand times that of uranium, was deprived of its accumulated emanation by solution in water and a rapid current of air. It was then allowed to stand air-tight for 105 minutes. The accumulated emanation now removed had an activity of 13·1 (in the same units as above). Find the radioactive constant for the decay of the emanation, and the ratio borne to the amount of emanation formed per second (1) by the emanation accumulated in the dry salt; (2) by the emanation accumulated in the solution during 105 minutes (equations (5) and (6), p. 279).

Answer $\frac{1}{480,000}$
(1) 480,000
(2) 6,300.

The ratio between the number of emanation atoms present after 105 minutes (N) and the number present at equilibrium (N_0) should first be found from the ratios of the activities.

The number formed per second n_0 is obtained on the assumption that the rate of formation is uniform during this relatively short time.

The required results follow at once from equations (5) and (6), p. 279.

Rutherford and Soddy (*Phil. Mag.*, April, 1903).

20. In general, the successive parts of a radioactive change may be disentangled by aid of the observation that different kinds of rays (α, β, or γ) are evolved by each change.

In the case of radium the changes: $Ra \longrightarrow$ emanation and emanation $\longrightarrow$ active deposit are each accompanied by the expulsion of an α particle. (See President. Address Brit. Ass., 1911, Sir W. Ramsay.)

One gram of radium at minimum activity (all emanation removed) expels $6{\cdot}2 \times 10^{10}$ α particles per second, and each expulsion means the change of one atom of radium.

One cubic centimetre of H_2 at $N.T.P.$ contains $3{\cdot}6 \times 10^{19}$ molecules (atomic weight of $Ra = 225$).

Find the "life" or time required for half transformation of radium; the fraction of the whole number of molecules changing in a year, and the time required to reduce any given amount in the ratio:

$$1 / 1 \times 10^{-6}.$$

Answer **1,280** years
5·36 × 10⁻⁴
29,800 years.

The number of mols. in gram mol. of H_2 = the number of atoms in gram atom of *Ra*. One gram of *Ra* contains

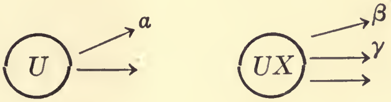
$$\frac{3{\cdot}6 \times 10^{19} \times 22{,}400}{225} = 3{\cdot}6 \times 10^{21} \text{ atoms.}$$

$$\frac{6{\cdot}2 \times 10^{10}}{3{\cdot}6 \times 10^{21}} = 1{\cdot}72 \times 10^{-11} = \text{fraction decomposing in 1 second.}$$

Hence the fraction of the original radium which decomposes in one second and in one year can be found. A knowledge of the fraction decomposing in one year allows of the evaluation of k (t in years) and also of the time required to half transform the radium.

Rutherford and Soddy (*Phil. Mag.*, April, 1903).

21. The radioactive changes of U into UX, with the emission of α rays, and of UX into the next product, with the emission of β and γ rays, are represented in the usual manner:



The changes may be followed separately, since the α rays, which produce most of the ionisation, may be cut off by a sheet of note-paper and are photographically inactive. The β rays easily pass through a sheet of paper, and have a strong photographic action.

Soddy (Trans. Chem. Soc. (1902), 81, 460); Rutherford and Grier (*Phil. Mag.*, September, 1902).

If N are the number of atoms of U, and N_X the number of atoms of UX present at radioactive equilibrium :

$$\text{Then}\qquad \left.\begin{aligned} -\frac{dN}{dt} &= kN \\ -\frac{dN_X}{dt} &= k_X N_X \end{aligned}\right\} \begin{array}{l} k \text{ and } k_X \text{ being the} \\ \text{radioactive constants} \\ \text{for the two changes.} \end{array}$$

$$\text{Also}\qquad -\frac{dN}{dt} = -\frac{dN_X}{dt}$$

The "life" or period of half-transformation of U into UX is 10^9 years, that of UX into the next product is 22 days.

Find the radioactive constants k and k_X (natural logs and t in years).

If there are 10^{24} atoms in 1 gram atom, find the number of atoms out of each gram atom of U which decompose in a year; also the normality with respect to UX of a solution in radioactive equilibrium, and normal with respect to U.

Ritzel (*Zeitsch. physikal Chem.* (1909), 67, 6).

Answer $k = 7 \times 10^{-10}$
$k_X = 12$
7×10^{14} atoms in each year.
1×10^{-10} normal with respect to UX.

Find the constants from the usual unimolecular equation, then note that $\frac{dN}{dt}$ is practically uniform in one year and is equal to $\frac{\Delta N}{\Delta t}$, or since the year is the unit, to ΔN which represents the number of molecules changed in a year.

Incomplete Reactions.

22. The reciprocal transformation of ammonium thiocyanate (NH_4CNS) into thiourea $(NH_2)_2CS$, and *vice versa*, has been investigated by Waddell (*Journ. Phys. Chem.* (1898), 2, 523) and by Reynolds and Werner (*Journ. Chem. Soc.* (1903), 83, 1).

(See also Walker and Hambly, *Journ. Chem. Soc.* (1895), 67, 746.)

The amounts x of thiocyanate had been transformed into thiourea at the end of the times given.

Find the constants for the direct and reverse reactions.

$t =$	0	19	38	48	60 minutes
$x =$	2·0	6·9	10·4	12·3	13·5

$\xi = 21{\cdot}2$ per cent. of thiocynate transformed.

The value of a at the beginning of the above experiment is evidently 98 per cent.

Answer $k_1 + k_2 =$ **0·0065** (**0·0068** from all results).
$k_1 =$ **0·0016.**

The sum of the constants $k_1 + k_2$ may be found from equation (6), p. 280, most rapidly by plotting the values of log $(\xi - x)$ against t. Results 2, 3, and 5 give the answer stated above. Afterwards k_1 may be found from equation (4).

23. A mixture was found to contain 5 per cent. of $(NH_2)_2CS$ and 95 per cent. of NH_4CNS at a given time. How much longer is required for 10 per cent. of the $(NH_2)_2CS$ to be transformed?

Answer **4·7** minutes.

(See equation (6a).)

24. The combination of formic acid with ethyl alcohol to form ethyl formate is another example of an incomplete reaction:

$$H{\cdot}COOH + C_2H_5OH \rightleftharpoons H{\cdot}COOC_2H_5 + H_2O.$$

In the presence of a large excess of alcohol and water the reaction is practically unimolecular, and the equations on pp. 279, 280, may be applied.

In the following results due to Kistiakowsky (*Zeitsch. physikal Chem.* (1898), 27, 250), x denotes the amount of formic acid esterified at the end of t minutes and ξ the amount transformed at equilibrium. The volume of the reacting mixture taken is the same throughout.

The mean value of the equilibrium constant $k = \frac{k_1}{k_2}$ (equation (7), p. 280) was found to be 1·60.

Plot the values of the logarithms of $(\xi - x)$ against t, and note that from the graph so obtained the amount of ester hydrolysed in a given time may be calculated.

Also evaluate the constant $k_1 + k_2$, find the initial amount of formic acid (a) present, and draw the graph for the esterification by plotting $a - \xi - x$ against t.

t	$\xi - x$
0	19·23
50	16·11
100	13·46
190	9·69
300	6·60

Answer $k_1 + k_2 =$ **0·001545**
$a =$ **31·25.**

Use equations (6) and (7).

25. From the data of the last problem calculate how long will be required to transform 10 per cent. of formic acid into ester and 10 per cent. of ethyl formate into formic acid, given that the initial concentration of each is the same as that found above (*i.e.*, 31·25 in the volume taken).

Answer **50** minutes for the esterification.
85 „ „ „ hydrolysis.

Equations (6) and (6A).

26. Draw a graph with the logarithms of unchanged formic acid as ordinates and the times as abscissæ, using the results already obtained; and compare this with the corresponding graph made by means of the constant k_1, on the assumption that the reaction goes completely from left to right.

How much acid will remain unchanged at the end of $t = 200$ minutes in the two cases?

Answer **21·46** and **20·18** in the units employed.

In the first case $\xi - x$ is found at $t = 200$ from the equation 4, p. 280, using $k_1 + k_2$, and hence $a - x$ may be obtained (since ξ and a are both known). In the second case $\log (a - x)$ is found in the usual manner, k_1 being taken as the constant of a unimolecular complete reaction.

27. $CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \rightleftharpoons CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO + H_2O$. Oxybutric acid is changed into its lactone at a certain velocity in the presence of hydrochloric acid. The concentration of the unchanged acid at any time is found by titration with baryta, the difference between the titre observed and that at the beginning being, of course, proportional to the amount of lactone formed.

P. Henry (*Zeitsch. physikal Chem.* (1892), 10, 96).

The concentration of the acid, after the lapse of t minutes, is expressed as cubic centimetres of a standard baryta solution required for a given volume.

At equilibrium the lactone formed = 13·28 cubic centimetres of $Ba(OH)_2$.

Find the velocity constant $k_1 + k_2$. (See equation (8), p. 280.)

t	c (acid)
0	18·23
21	15·84
50	13·25
80	11·09
120	9·35
220	6·67
320	5·66
∞	4·95

Answer $k_1 + k_2 =$ **0·00411** (mean value).

The equilibrium constant K must first be found from the above results.

The velocity curves for the lactone formation and hydrolysis may be plotted exactly as in the last problem.

28. In cases of bimolecular reactions, such as that given below, $\frac{dC}{dt}$ at the beginning of the direct and reverse reactions, and therefore k_1 and k_2, may be obtained with sufficient accuracy from the mean values of $\frac{\Delta C}{\Delta t}$ over several time intervals near the beginnings of the reactions. During these times the concentrations of the resultants (right or left hand components) are still negligibly small compared to those of the reactants (left or right hand components).

From the following results of Knoblauch (*Zeitsch. physikal Chem.* (1897), 22, 268), find the velocity constants of the direct and reverse reactions, and the equilibrium constant for the whole reaction.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

Esterification.

Left to right.

Initial concentration, 1 mol. CH_3COOH per litre ; 12·756 mols. C_2H_5OH per litre.

t (minutes)	C (ester)
0	0·0
44	0·1327
53	0·1628
62	0·1847

Hydrolysis of ester.

Right to left.

Initial concentration, 1 mol. $CH_3COOC_2H_5$ per litre ; 12·215 mols. H_2O per litre.

t (minutes)	C (acid)
0	0·0
78	0·0777
86	0·0862
94	0·0930

$$\text{Answer} \quad k_1 = 0{\cdot}000238$$
$$k_2 = 0{\cdot}0000815$$
$$K = 2{\cdot}92.$$

The mean values of the velocities $\frac{\Delta C}{\Delta t}$ of the direct and reverse reactions over the time intervals 0 – 44, 0 – 78, etc., are 0·00302 and 0·000996, respectively.

Hence k_1 and k_2 may be found from equation (10) (Introduction, p. 281).

Compare the value of K with that directly determined.

29. Using the data of the preceding problem, find the velocity of the transformation at the moment when the amount of acid and alcohol transformed is equal to one half the amount which would be transformed at equilibrium. Also compare this velocity with the velocity which would prevail at the same concentrations of the reacting substances, if there were no opposing reaction.

$$\text{Answer} \quad \frac{dx}{dt} \text{ (with opposing action)} = 0{\cdot}001483$$
$$\frac{dx}{dt} \text{ (without opposing action)} = 0{\cdot}001502.$$

The amount transformed at equilibrium in a mixture of m molecules of one reactant, with one molecule of the other reactant may be determined from the equation (11), p. 281.

$$\text{Hence} \quad \xi = \frac{(1+m)K + \sqrt{K^2(m+1)^2 - 4mK^2(K-1)}}{2\,(K-1)}.$$

(See p. 149.)

$$\text{and} \qquad \frac{dx}{dt} = k_1\left(1 - \frac{\xi}{2}\right)\left(m - \frac{\xi}{2}\right) - k_2\left(\frac{\xi}{2}\right)^2$$

in the case mentioned above.

30. What percentage of the total molecules in the above mixture are transformed in both directions, at equilibrium in the course of 1,000 minutes ? ”

Answer **1·14** per cent.

Consider 1 litre of the mixture.

$$\frac{dx}{dt} \text{ is uniform and therefore equal to } \frac{\Delta x}{\Delta t}.$$

$$\frac{\Delta x}{\Delta t} \text{ (mols. per min.)} = k_1(1 - \xi)(m - \xi) = k_2\xi^2.$$

Total amount transformed in both directions

$$= \frac{\Delta x}{\Delta t} \times t \times 2.$$

31. The reaction:

$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ can be much accelerated by the addition of dilute HCl.

For the right to left reaction:

$\frac{dx}{dt} = k_2(C_1 - x)(C_2 - x) - k_1(C'_1 + x)x$, C_1, C_2 and C'_1, being the initial concentrations of water, ester and alcohol.

If C_1 and C'_1 are large in comparison to C_2, the former concentrations may be taken as constant;

and $$\frac{dx}{dt} = k_2[C_1(C_2 - x) - kC'_1x],$$

putting $K = \frac{k_1}{k_2}$, and rejecting powers of C_2 and x higher than the first.

The integration of the above equation gives:

$$k_2 = \frac{2{\cdot}3}{t(C_1 + KC'_1)} \log \frac{C_1C_2}{C_1C_2 - (C_1 + KC'_1)x}$$

A mixture is made of 100 grams of dilute aqueous HCl ($D = 1$), 100 grams of C_2H_5OH ($D = 0{\cdot}81$) and 10 grams of $CH_3COOC_2H_5$ ($D = 0{\cdot}905$). The density of the mixture is found to be 0·934.

The equilibrium constant $K = \frac{k_1}{k_2}$ is 4. Find the velocity constants of the two reactions, and the amounts of each of the four substances present at equilibrium, given that one-fifth of the ester is transformed in 51·82 days.

First calculate the concentrations of all the reacting molecules, expressed as molecules per 100 cubic centimetres of the mixture.

Thus C (water) $= \dfrac{100 \times 1}{18 \times 225} = 0{\cdot}02469.$

Then calculate k_2 as above, k_1 by means of K and the quantities transformed by the equation given on p. 302.

$$k_2 = \frac{2{\cdot}3}{51{\cdot}82 \times 5{\cdot}52} \times 0{\cdot}2572.$$

Answer $k_2 = \mathbf{0{\cdot}002607.}$
$k_1 = \mathbf{0{\cdot}010428.}$

32. How many molecules of ester are produced when $m = 0{\cdot}05$, $1{\cdot}0$ and $8{\cdot}0$ of alcohol are mixed with one molecule of acetic acid?

$$K = 4.$$

Answer **0·0404.**
0·667.
0·966.

Use equation in Problem 31, p. 301.
See Mellor ("Chemical Statics," pp. 147, 80).

Order of a Reaction.

33. It has been found by the differential method that cyanic acid $HCNO$ (gas) polymerises to cyamelide $(HCNO)_3$ (solid with a negligible vapour pressure), according to the equation:

$$3\,HCNO = (HCNO)_3$$

Van't Hoff, "Chemical Dynamics."

In calculating the value of n (= 3) the pressures of the disappearing gas were used throughout, instead of the concentrations to which they are proportional.

The pressure of a sample of $HCNO$, kept in a vessel at constant volume fell from 188·84 millimetres to 153·46 millimetres in 23 hours. Hence, find the fall in pressure of a similar sample, kept in the same vessel for 20 hours; the initial pressure being 79·07 millimetres.

Answer **76·81** millimetres.

Use equation (1), p. 282.

34. A reaction is known to be of the fourth order. The time required to transform 3 molecules of the reacting substance, which is present in the concentration of 15 molecules in 10 litres, is two hours. In what time will 6 molecules be transformed out of a mixture containing 30 molecules in 10 litres?

Answer $t =$ **15** minutes.

35. Ferrous chloride is oxidised to ferric chloride by potassium chlorate, in the presence of hydrochloric acid.

The initial concentrations of $FeCl_2$, $KClO_3$ and HCl were each 0·1, and the course of the reaction was followed by the titration of $FeCl_3$, which gives $x =$ the change in concentration of the reacting substances during each interval.

	Time	x
(1)	0 — 5	0·0048
(2)	5 — 15	0·0122
(3)	35	0·0238
(4)	60	0·0329
(5)	110	0·0452
(6)	170	0·0525

Determine the order of the reaction by the method of last problems.

From results (1) and (2) combined with (5) and (6):

$$n = \mathbf{3{\cdot}29}.$$

Therefore the reaction is probably of the third order.

36. Apply method (2) (p. 282) to determine the order of the reaction between $FeCl_3$ and $SnCl_2$, to form $FeCl_2$ and $SnCl_4$ in aqueous solution, using the ratios:

$$\frac{C_1 - C'_1}{C_1} = \tfrac{1}{3}, 0{\cdot}5, 0{\cdot}7.$$

$C_1 = 0{\cdot}10$		$C_2 = 0{\cdot}0625$	
Time	$C_1 - C'_1$	Time	$C_2 - C'_2$
0·75	0·0359	1·0	0·01434
1·0	0·0419	1·75	0·01998
1·5	0·0510	3·0	0·02586
2·5	0·0618	4·5	0·0308
4·0	0·0700	7·0	0·0361
6·5	0·077	11·0	0·0410
		17·0	0·0450

Noyes (*Zeitsch. physikal Chem.* (1896), 19, 599).

Answer $n =$ **3·12, 3·41, 3·10.**

From many other values it appears that:

$$2\ FeCl_3 + SnCl_2 = 2\ FeCl_2 + SnCl_4$$

represents the mechanism of the reaction.

Note.—In order to obtain fractional decreases of concentration equal to $\frac{1}{2}$, etc., in the case of the two concentrations, it is necessary to interpolate the experimental results. This is best done by plotting on squared paper.

37. The acids HBr and $HBrO_3$ react in aqueous solution to form Br_2 and H_2O. The order of the reaction with a mixture of the pure acids alone differs from that taking place with a mixture containing excess of H_2SO_4.

Judson and Walker (*Journ. Chem. Soc.* (1898), 73, 410).
Ostwald (*Zeitsch physikal Chem.* (1888), II., 136).
Meyerhoffer („ „ „ „ „ 585).

The reaction consists in the formation of $HBrO$ and $HBrO_2$ followed by a rapid reaction between these and HBr. In this, as in other cases, it is the velocity of the slower reaction which is actually measured.

In the following the concentrations of the acids (C) and of Br_2 formed (x) are expressed in cubic centimetres of a standard thiosulphate solution required to reduce the iodine set free from the potassium iodide by the bromine formed in the reaction.

	C	t_1	C	t_2
(1)	77·0	0	51·33	0
	51·33	15	34·22	50
	$C_o = 77$		x	t
			25·1	15·0
(2)			28·7	20·0

Find the order of the reaction, and its velocity constant; also write the ionic equation for the formation of $HBrO$ and $HBrO_2$, and state what is probably the order of the same reaction, in the presence of excess of H_2SO_4.

Answer $n = \mathbf{4}$

$k = \mathbf{0{\cdot}0_6110}$ and $\mathbf{0{\cdot}0_6111}$

$$2\,H^{\cdot} + Br' + BrO'_3 = HBrO + HBrO_2.$$

The second order in the presence of excess of H_2SO_4. The order may be found by the method (2) (Introduction, p. 282), from results (1), and k, from results (2). When the reaction takes place in the presence of excess of H_2SO_4, the hydrogen ion concentration is much greater than that of the changing molecules, and remains practically constant.

Velocity of Diffusion.

38. A ball of copper was rotated in nitric acid ($D = 1{\cdot}71$), and weighed from time to time. During the first second the weight decreased from 4·3465 to 4·0463 grams; during the second second from 4·0463 to 3·7673 grams, the average surfaces during these time intervals bêing 289·93 and 276·4 centimetres squared.

What is the average attack on a square metre of surface, and what will be the decrease of weight during the sixth second if the velocity remains constant (as was found to be the case) and the surface is now reduced to 225·15 $(cm)^2$?

Answer **10·22** grams.

0·23 „

Veley (*Journ. Chem. Soc.* (1889), 55, 361).

39. The action of acids upon marble and other carbonates has been investigated by Spring (*Zeitsch. physikal Chem.* (1888), 13, 2).

The decrease of acid concentration may be determined by titration, or by measuring the CO_2 evolved.

Some solid carbonate with constant surface immersed in $N.\ HCl$ is found to be attacked at the rate of 0·091 milli-equivalent per second, at the time when the acid has lost one quarter of its titre.

What will be the length of time required to produce this fall of concentration if the thickness of the diffusing layer on the surface of the marble remains constant?

First determine k, equation (5), p. 284.

$C_S - C$ being 0·75, then make $C_S - C = 1{\cdot}0$, and solve for t, in equation (6).

Answer **0·000121** equivalents per second.

$t =$ **39 minutes, 32 seconds.**

40. The rates of solution of benzoic acid and lead chloride were each found to be controlled by the rate of diffusion from the film of saturated solution surrounding the solids. (Noyes and Whitney, *Journ. Amer. Chem. Soc.* (1897), 19, 930.)

The solubility of $PbCl_2$ is 38·66 millimols. per litre, at 25°. In 10½ minutes 6·14 millimols., and in 1 hour, 24·58 millimols. are dissolved from a constant surface, rotating at constant speed, in a constant volume of the solution. From the mean velocity constant, find the time required to arrive within 10 per cent. of saturation.

Answer $t =$ **2 hours, 0 minutes, 19 seconds.**

Use the integrated form, equation (6), p. 284.

41. A piece of marble ($CaCO_3$), having a constant surface dissolves initially at the rate of 5 grams per minute, in one litre of normal HCl which is stirred at a constant rate. Find what volume of CO_2 (at N. T. P.) will be evolved in 20 minutes.

Also, in how many minutes will the same volume of gas be evolved from an identical piece of marble in 2 litres of the same acid.

Answer **9·84** litres.
10·96 minutes.

The constant $k = \frac{k_D S}{lV}$ may be found (equations 5, 6), either from the integrated equation, or from the method of finite differences.

If the latter method is used, and Δc is the small decrease in concentration during the time Δt, then the average concentration during Δt is $C + \frac{1}{2}\Delta c$,

and
$$k = \frac{\Delta c}{C - \frac{1}{2}\Delta c}.$$

The decrease in the acid concentration ΔC may of course be obtained from a knowledge of the molecular weight of $CaCO_3$ (1 molecule = 2 equivalents).

The value of k by the latter method is 0·1052, by the former 0·1054.

The value of $C_S - C$ after 20 minutes may now be obtained in the usual manner, hence, C (in equivalents) and the volume of CO_2.

With 2 litres of the acid, the constant $\frac{k_D S}{Vl}$ becomes $\frac{0·1054}{2} = 0·0527.$

The 0·8785 equivalents of marble dissolved now, however, only reduce the concentration of the acid to 0·5608.

Compare also the times required to produce the same decreases of concentration in the 1 and 2 litres of acid.

42. The surface of the marble in the preceding problem was 20 $(cm)^2$. If the diffusion coefficient k_D of HCl is taken as 2·0 in round numbers, expressed in $(cm)^2$ days, find the thickness (in μ) of the diffusing film on the surface of the marble.

Answer $l = \mathbf{0{\cdot}44}\ \mu$.

k_D, the diffusion coefficient given must be reduced to equivalents diffusing in one minute.

$$k_D = \frac{2{\cdot}0}{1{,}440 \times 60} \text{ in } (cm)^2 \text{ minutes.}$$

$$K = \frac{k_D S}{Vl} = 0{\cdot}1054, \qquad \frac{k_D}{l} = \frac{105{\cdot}4}{20}.$$

43. A surface of fused benzoic acid having an area of $S = 18\ (cm)^2$ is immersed in water, stirred at a constant rate. It is assumed that by this means the thickness l of the surface film is kept constant.

The concentrations of benzoic acid (expressed in millimols. per litre) were obtained by the titration of 20 c.c., removed at the beginning and end of each time interval, Δt minutes.

The volumes of the liquid are given in the third column of the table below.

Find the mean value of the constant $\frac{k_D S}{Vl}$, if the unit of the dissolving surface is 20 $(cm)^2$, and the saturation concentration is 24·3 millimols. per litre.

Answer **2·3**.

Δt	C	V
	0·75	
12		1,020 c.c.
	2·05	
15		1,000
	3·75	
13·3		980
	5·05	

Use Equation (6).

The three values of $\frac{k_D}{2{\cdot}303l}$ are:

2·05, 2·30, 2·05.

Brunner (*Zeitsch. physikal Chem.* (1904), 47, 56).

44. The diffusion constant k_D of benzoic acid in water (see equation (1), p. 283, is found to be 0·75. It is expressed as grams per $(cm)^2$ per day, diffusing down a concentration gradient of 1 gram per centimetre.

Find the thickness l of the surface film expressed in μ (0·001 mm.) (see last problem).

Answer $l =$ **20** μ.

Note.—The diffusion coefficient must be multiplied by the appropriate factor to reduce it from days to minutes.

Since the concentration gradient is expressed in centimetres, these must be multiplied by the proper factor to reduce them to μ.

45. The following are the results of an investigation into the rate of solution of alabaster ($CaSO_4$) in water, at 25°, when stirred at the constant rate of 2,235 revolutions per minute.

Bruner and Tolloczko (*Zeitsch. anorg. Chem.* (1903), 35, 39).

It is to be noted that the rate of solution increased continually with the rate of stirring, without attaining a maximum. The thickness of the surface film as calculated below only holds good, therefore, for that particular rate.

Volume of solution = 1 litre.
Surface of alabaster = 31·55 $(cm)^2$.

Saturation concentration = 0·1047 grams of $CaSO_4$ in 50 c.c.

t (hours)	C (grams in 50 c.c.)
0	0·0004
0·083	0·0274
0·167	0·0492
0·200	0·0566
0	0·0270
0·083	0·0480
0·167	0·0632
0·25	0·0736

Find the constant for the particular reaction, *i.e.* $\frac{k_D}{Vl}$ (equation (5)).

Answer **0·0512.**

The diffusion constant of $CaSO_4$ may be calculated from the ionic mobilities by means of the formula (Nernst):

$$K = 0{\cdot}04485 \frac{u_A u_K}{u_A + u_K} [1 + 0{\cdot}0034 (t - 18)] \frac{(cm)^2}{\text{days.}}.$$

46. The value of k_D in these units is 1·45. Find the thickness of the diffusing film of $CaSO_4$ by means of the constant previously obtained.

Answer $l =$ **5·0** μ.

See preceding problems. The mean value of $\frac{k_D}{2{\cdot}303\,Vl}$ for 1 $(cm)^2$ of surface is first determined from the experimental data; hence $\frac{k_D}{l}$ (V in c.c.). The diffusion constant is then reduced from days to hours and "l" obtained in centimetres.

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